Physics Lib

VOLUME 28 SECOND SERIES NUMBER 5

THE PHYSICAL REVIEW

A JOURNAL OF EXPERIMENTAL AND THEORETICAL PHYSICS

CONDUCTED BY

THE AMERICAN PHYSICAL SOCIETY

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PUBLISHED BY THE AMERICAN PHYSICAL SOCIETY

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Second Series *November, 1926* *Vol. 28, No. 5*

THE

PHYSICAL REVIEW

HIGH FREQUENCY RAYS OF COSMIC ORIGIN III. MEASUREMENTS IN SNOW-FED LAKES AT HIGH ALTITUDES

By R. A. Millikan and G. Harvey Cameron

Abstract

1. **Absorption experiments in Muir Lake (alt. 11,800 feet).**—The sinking of sealed electroscope No. 3 in Muir Lake showed an ionization decreasing steadily with depth from 13.3 ions per cc per sec. at the surface to 3.6 ions at 50 feet below the surface, below which there was no further decrease. The absorption curve of electroscope No. 3 was in excellent agreement with that of No. 1.

2. **Absorption experiments in Arrowhead Lake (alt. 5,100 feet).**—The electroscope readings in Arrowhead Lake correspond uniformly to readings six feet deeper in Muir Lake. This difference is the exact water equivalent of the absorption of the atmosphere between the two elevations. All readings of both electroscopes fit satisfactorily upon a single curve relating ionization to depth beneath the surface of the atmosphere in equivalent meters of water.

3. **Rays of cosmic origin.**—1 and 2 combined with the failure to detect any systematic diurnal variation, in tests of a number of days duration at high altitudes, constitute new and quite unambiguous evidence for the existence of very hard etherial rays of cosmic origin entering the earth uniformly from all directions.

4. **Spectral distribution of cosmic rays.**—No single absorption coefficient is found to fit the absorption curve, the lower end of which requires a coefficient of .18 per meter of water; the upper end a coefficient, .30 per meter of water. These coefficients correspond, by Compton's equations, to wave-lengths $\lambda = .00038$A and $\lambda = .00063$A. These are fifty times the frequencies of ordinary gamma rays, $\lambda = .025$A, and the former corresponds to an energy of 32,000,000 volts.

5. **Number of pairs of ions due to cosmic rays.**—The observed number of pairs of ions in electroscope No. 1 due to cosmic rays is about 1.4 at sea level, 2.6 at 1600 meters, 4.8 at 3600 meters, 5.9 at 4300 meters.

6. **Stimulated secondary rays.**—Theoretically, cosmic rays of the foregoing energy should not stimulate ether waves of gamma ray hardness, but should produce beta rays capable of penetrating brass walls 5 mm thick. The observations present evidence of rays of about this hardness increasing systematically with altitude in rough proportionality to the intensity of the cosmic rays. This evidence is not completely convincing because of inability thus far to eliminate the effects of the gamma rays from the underlying rocks.

7. **Origin of cosmic rays.**—Evidence is presented that these rays do not result from the union of protons with negative electrons, but they are rather

due to nuclear changes of about one-thirtieth the energy corresponding to such union, taking place throughout the depths of the universe.

I. Introduction

THE 1922, high altitude, sounding balloon flights reported in Part I[1] had shown that some sort of a penetrating radiation exists in the upper reaches of the atmosphere, though of not more than one fourth the intensity theretofore reported. Again, the 1923 absorption experiments on mountain peaks reported in Part II[2] had shown that there exists at such heights a new radiation of local origin and of something like gamma ray hardness, but they had seemed to prove conclusively that if rays of *cosmic origin* exist at all they must be of somewhat different characteristics from any as yet suggested.

Up to the time of the Pikes Peak observations (September, 1923) the only work which had appeared demanding an absorption coefficient smaller than $5\times10^{-3}\text{cm}^{-1}$ for cosmic rays, if they existed, was the aforementioned sounding balloon experiments of Millikan and Bowen performed in April, 1922.[1] However, at the sitting of December 20, 1923, of the Preussischen Akademie der Wissenschaften Dr. Werner Kolhörster presented the results of new experiments, the first of which consisted in sinking electroscopes in different bodies of water at about sea level and observing a slight decrease in the number of ions as compared with the surface value. He attributed the noticeable lack of concordance between the results in the different bodies of water experimented upon to the different influences of the banks, but even with a CO_2 filling of the electroscopes the maximum change produced by sinking in water amounted to 2.1 ions, which would presumably be about 10 percent of the normal surface reading (not recorded in the report).

Dr. Kolhörster's comments upon these observations are as follows. "From the lake-experiments there results the absorption coefficient $\mu=2\times10^{-3}\text{cm}^{-1}$, while my former balloon experiments gave $5\times10^{-3}\text{cm}^{-1}$, a satisfactory agreement in view of the small intensity, about 2 ions, with which the penetrating rays reach the earth," thus indicating that these measurements were not sufficiently certain, in his judgment, to differentiate between $\mu=5\times10^{-3}$ and $\mu=2\times10^{-3}$.

He next made observations in crevasses in glaciers at altitudes of 2300 m and 3500 m on the Jungfrau, and obtained in three experiments for μ $1.6\times10^{-3}\text{cm}^{-1}$, $2.6\times10^{-3}\text{cm}^{-1}$, and $2.7\times10^{-3}\text{cm}^{-1}$. Combining

[1] Millikan and Bowen, Carnegie Institution Year Book, No. 21, 386 (1922); also Phys. Rev. 22, 198 (1923) and 27, 353 (1926).

[2] Millikan and Otis, Phys. Rev. 27, 645 (1926).

these three observations on equal footing with those made in water and reported above, he recorded as the rough mean of the four observations $\mu = 2.5 \times 10^{-3} cm^{-1}$, a figure, however, now so low as to be no longer incompatible with the Kelly Field sounding balloon experiments.[1]

Finally, after having quoted the value of μ for the hardest gamma rays from RaC as $3.9 \times 10^{-2} cm^{-1}$, and from ThD as $3.3 \times 10^{-2} cm^{-1}$, he summarizes his paper thus: "To resume, it is to be emphasized that the existence of a hard gamma ray with an absorption coefficient about 1/10 that of the hardest known gamma rays has been demonstrated." The final value chosen was thus about the linear mean of all the observations taken, from 1.6 up to 5.7, namely, about $3.3 \times 10^{-3} cm^{-1}$. Also, in a very recent paper[3] Dr. Kolhörster again holds that all his observations upon mountains have confirmed the results of his balloon observations, while Hess[4] also holds that the result obtained in Kolhörster's balloon-flights is more trustworthy than that given by Millikan and Bowen's 1922, sounding balloon observations.

The Pike's Peak work of Millikan and Otis[2] had shown, however, (1) that the *mean* absorption coefficient of the rays found on top of the peak was only about that of ThD, and (2) that cosmic rays producing 2 ions per cc at the earth's surface and having an absorption coefficient even as low as $\mu = 2.5 \times 10^{-3} cm^{-1}$, although no longer in conflict with the sounding balloon experiments would of necessity have produced a 50% larger change inside lead screens in going from sea level to Pikes Peak than that they observed. They concluded, therefore, that cosmic rays *of the assumed characteristics did not exist.* If any of the penetrating rays were of cosmic origin they had to be still harder. The whole of the Pikes Peak data could in fact be explained without them. Accordingly we planned for the summer of 1925 new experiments designed:

(1) To settle definitely the question of the existence or non-existence of a small, very penetrating radiation of cosmic origin—a radiation so hard as to be uninfluenced by, and hence unobservable with the aid of, such screens as we had taken to Pikes Peak; and

(2) To throw light on the cause of the variation with altitude of the radiation of about gamma-ray hardness which our absorption experiments on Pikes Peak showed to be more than twice as copious there as at Pasadena.

The only possible absorbing material obtainable in the immense quantities needed, and of homogeneous and non-radioactive constitution, were the waters of very deep snow-fed lakes—snow-fed because the

[3] Kolhörster, Die Naturwissenschaften **15**, 31, 426.
[4] Hess, Phys. Zeits. **27**, 405 (1926).

results of under-water experiments which we had previously carried on near Pasadena had been vitiated by our discovery that the waters were appreciably radioactive. We felt that there was much uncertainty as to how much this cause might have affected the European observations in and about glaciers. Further, since the Pikes Peak experiments had demonstrated that if any of the penetrating rays were of *cosmic origin*, the ionization due to them in our electroscope at sea level had to be less than the 2 ions, assumed above, out of the 11.6 observed, the experimental error being, say, half an ion, no crucial tests could possibly be made unless we could find very deep, non-radioactive lakes at very high altitudes where cosmic rays, if they existed, had two or three times the ionizing effect to be expected from them at sea level. We needed at the least three or four ions due to cosmic rays, to vary with absorbing materials, if we were to obtain *unambiguous* evidence.

II. The Electroscopes

The two electroscopes used in these experiments are shown in Fig. 1. Electroscope No. 1 is the same as that used in the experiments described

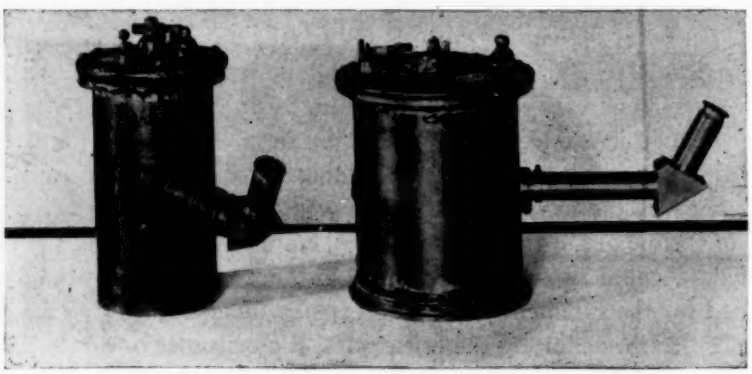

Fig. 1. Photograph of electroscopes 1 and 3.

in Part II,[2] but with new fibres inserted, while electroscope No. 3 is a new one very much like the first save that it had a greater sensitivity because of a larger volume and a smaller electrical capacity. It was 29.5 cm high and 15 cm in diameter. It was built entirely of brass, side walls 3 mm thick, and had a volume of 3211 cc, 1.69 times that of No. 1. The electrical capacity of No. 3 was 1.10 e.s. units, as measured by the method of mixed capacities, a small condenser the capacity of which (15.85 e.s. units) could be computed accurately from its dimensions being used as a standard. The capacity of No. 1, as remeasured for the purposes of

these experiments, was 1.41 electrostatic units. The method of measurement was precisely that described in Part II except that much longer periods of observation, from 5 to 14 hours, were generally used. As described in Part II a calibration curve was drawn for each reading to avoid errors due to changing characteristics of the instrument. That saturation was obtained was shown by the fact that for long observations in which the potential fell from say 200 volts to 50 volts the ionization was not appreciably less than when, with the same external radiation, the fall of potential was from 200 to 150 volts.

III. Experiments in Muir Lake and Arrowhead Lake

The foregoing electroscopes were taken first to Muir Lake, 11,800 feet above sea level, just under the brow of Mount Whitney, the highest peak in the United States, a beautiful snow-fed lake hundreds of feet deep and some 2000 feet in diameter. Here we worked for the last ten days in August, 1925, sinking our electroscopes to various depths down to 67 feet. *Our experiments brought to light altogether unambiguously a radiation of such extraordinary penetrating power that the electroscope-readings kept decreasing down to a depth of 50 feet below the surface.* The atmosphere above the lake was equivalent in absorbing power to 23 feet of water, so that here were rays so penetrating that, if they came from outside the atmosphere, they had the power of passing through $50+23=73$ feet of water, or the equivalent of 6 feet of lead, before being completely absorbed. The most penetrating x-rays that we produce in our hospitals cannot go through half an inch of lead. Here were rays at least a hundred times more penetrating than these. This was in agreement qualitatively with Kolhörster's 1923 contention. The absorption coefficient however came out but one twentieth, instead of "about one-tenth of that of the hardest known gamma rays,"[5] and the number of ions at sea level was but 1.37 (see below).

How unambiguous was now the experimental evidence may be seen from the fact that with the aid of the new electroscope of high sensitivity (because of small capacity and large volume) the change in ions per cc per sec. in going from the surface of Muir Lake to the depth of 15 meters (50 feet) was from 13.3 ions to 3.6 ions, or a decrease to about a fourth value. Since the largest decrease below a surface reading reported by Kolhörster due to sinking electroscopes in water[5] was 2.1 ions, or a decrease of probably about 10%, we seem here to have obtained an altogether new precision of measurement and unambiguity of evidence.

[5] Kolhörster, Sitz.-Ber. Preuss. Akad. Wiss. **34**, 366 (1923).

To obtain definite evidence as to whether these very hard rays were however *of cosmic origin*, coming in wholly from above and using the atmosphere merely as an absorbing blanket, we next went to another very deep snow-fed lake, Lake Arrowhead in the San Bernardino mountains, 300 miles farther south and 6700 feet lower in altitude, where the Arrowhead Development Company kindly put all their facilities at our disposal. The atmosphere between the two altitudes has an absorbing power equivalent to about 6 feet of water. *Within the limits of observational error, every reading in Arrowhead Lake corresponded to a reading 6 feet farther down in Muir Lake, thus showing that the rays do come in definitely from above, and that their origin is entirely outside the layer of atmosphere between the levels of the two lakes.* This, taken together with the sounding-balloon data, appears to eliminate completely the idea that the penetrating rays may have their origins in thunder-storms, a possibility recently suggested by C. T. R. Wilson and repeated by Eddington.[6]

The procedure in taking these readings was to take the electroscopes out in a canvass army boat, carried part way up to the lake by pack animals and partly by ourselves, to sink both electroscopes side by side at the chosen depth, and leave them so immersed for a period of from 6 to 14 hours. We could usually obtain but two readings in 24 hours. The process of taking and of treating these readings was precisely that described in II. The elaborate precautions for eliminating leak over the supporting quartz rod were not used because they were found to make no change in the rate of discharge.

Table I

Readings in Lakes Muir and Arrowhead

				Electroscope No. 3					
				Muir Lake					
Depth below surface (m)	0	.45	1.0	2.8	3.0	5.0	10.0	15.0	20.0
Ionization	13.3	9.7	7.7	6.0	5.45	4.9	4.0	3.6	3.6
(ions/cc/sec)	13.2	....	7.8	5.8	....	4.6	4.0	....	3.7
Means	13.25	9.7	7.75	*5.9* ↓	*5.45* ↓	*4.75* ↓	4.0	3.6	3.65
				Arrowhead					
Depth below surface (m)	0	.7	1.0	1.1	3.0	5.0	....	15.0	....
Ionization	7.0	5.8	5.5	5.15	4.85	4.4	....	3.7	....
(ions/cc/sec)	7.2	....	....	....	4.9	....	....	....	....
	7.5	....	....	....	....	....	....	....	....
	6.9	....	....	....	....	....	....	....	....
	7.2	....	....	....	....	....	....	....	....
Means	7.0	↑ *5.8*	↑ *5.5*	5.15	↑ *4.9*	4.4	....	3.7	....

[6] Eddington, Nature Supplement, May 1, 1926, p. 32.

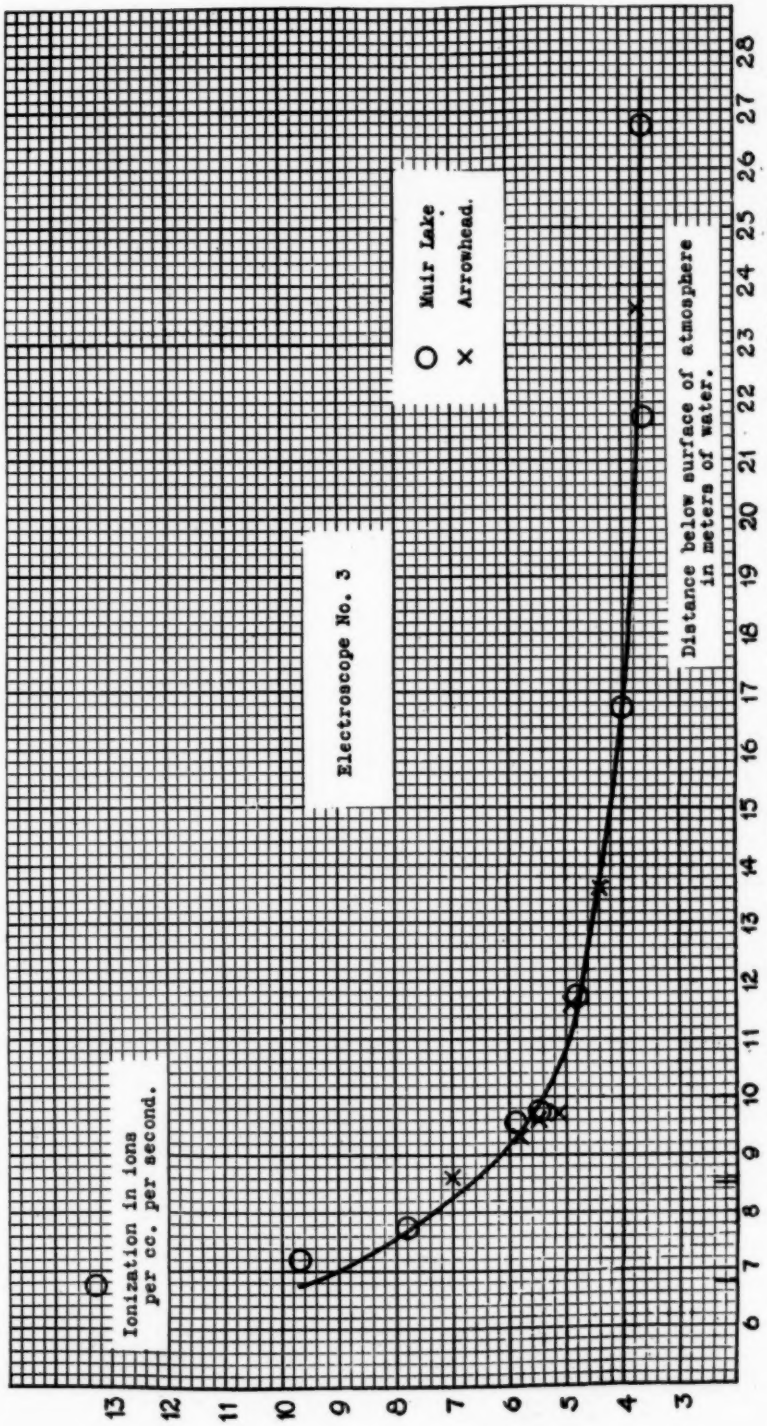
Ionization in ions per cc. per second.
Electroscope No. 3
Muir Lake
Arrowhead.
Distance below surface of atmosphere in meters of water.

Fig. 2. Variation of the ionization in Electroscope No. 3 with depth below the surface of the atmosphere.

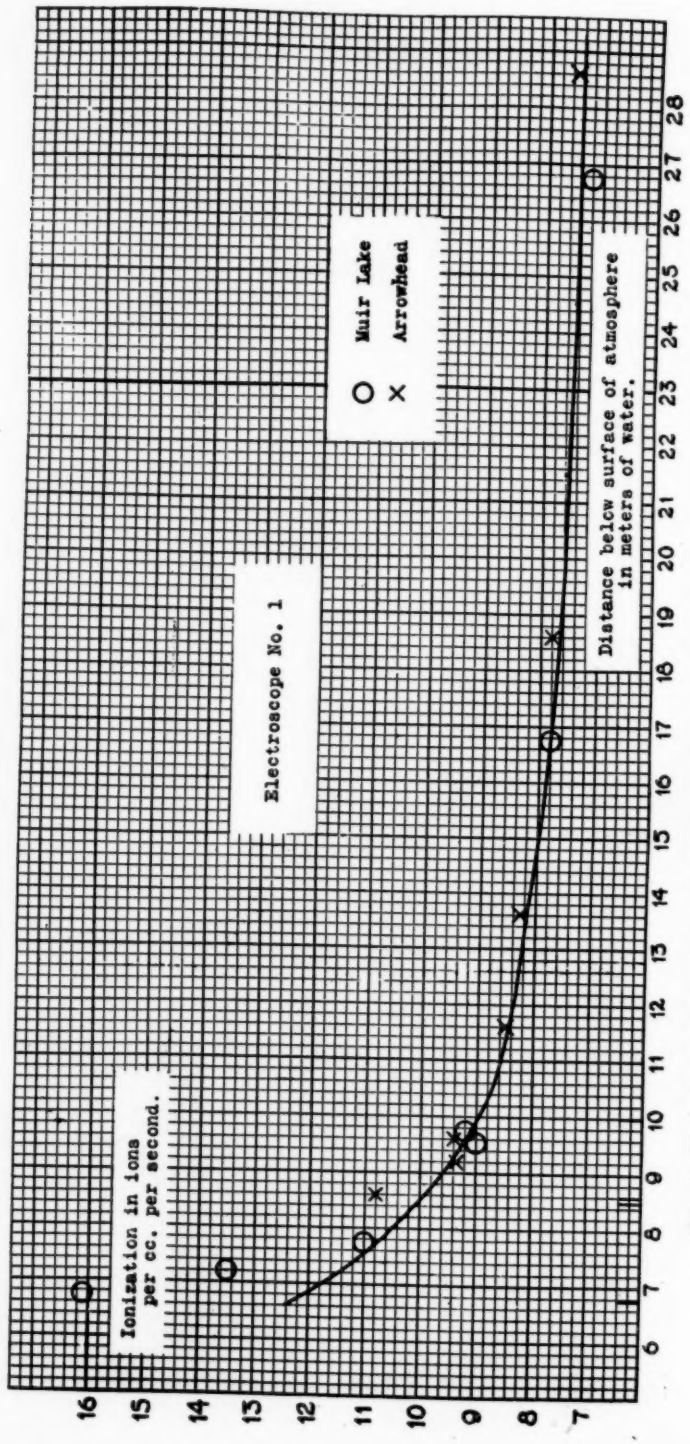

Fig. 3. Variation of the ionization in Electroscope No. 1 with depth below the surface of the atmosphere.

Electroscope No. 1
Muir Lake

Depth below surface (m)	0	.45	1.0	2.8	3.0	....	10.0	....	20.0
Ionization (ions/cc/sec)	16.5	13.5	11.0	9.0	9.2	....	7.8	....	7.2
	15.8	....	....	....	..	....	....	....	....
	15.9	....	....	....	....	....	....	....	....
Means	16.1	13.5	11.0	9.0	9.2 ↙	....	7.8	....	7.2

Arrowhead

Depth below surface (m)	0	.6	1.0	....	3.0	5.0	10.0		20.0
Ionization (ions/cc/sec)	10.5	9.35	9.6	....	8.6	8.3	7.8	....	7.5
	11.0	....	9.2	....	8.45	....	....	....	....
Means	10.75	9.35	↗ 9.4	....	8.5	8.3	7.8	....	7.5

Table I shows all of the readings taken in Lake Muir and Lake Arrowhead. The arrows connect or point toward readings taken at the same depth beneath the top of the atmosphere, and it will be seen that they are all the same within the limits of error whether taken in Lake Muir or Lake Arrowhead.

Figs. 2 and 3 show the curves obtained by plotting all the readings taken in the two lakes as ordinates, and as abscissas the depths in meters beneath the top surface of the atmosphere, reduced to the equivalent depth beneath water. These depths were computed with the aid of the mean temperatures, as a function of altitude, given in the Smithsonian Tables. On these graphs the "depth" beneath the top of the atmosphere of the surface of Muir Lake is 6.75 m, that of Arrowhead Lake 8.6 m, that of Lone Pine 8.5 m, and that of Pasadena 9.98 m. It will be seen that all of the readings corresponding to points more than half a meter beneath the surface of the water fall upon a smooth curve. The fact that readings taken above the surface are all above the curve is due to the presence above the surface in addition to the penetrating radiation of a local radiation of ordinary penetration. Since this latter radiation is all absorbed in a meter or less of water, the points corresponding to depths equal to half a meter are all on the smooth cosmic radiation curve, while those corresponding to readings at the surface are above this curve.

Analysis of these absorption curves shows that the rays are not homogeneous but are hardened as they go through the atmosphere, just as x-rays are hardened by being filtered through a lead screen. Our hardest observed rays have an absorption coefficient of 0.18 per meter of water, and the softest which get down to Muir Lake a coefficient of 0.3 per meter. The sounding balloon experiments of Millikan and Bowen make it improbable that they become very much softer than this at the top of the atmosphere, since otherwise these observers should have obtained larger readings in their very high flight.

Observations carried on by Millikan and Otis day and night for several days on Pikes Peak at an altitude of 14,100 feet, and for two consecutive days on Mount Whitney at an altitude of 13,500 feet had revealed no preferential direction in the heavens from which the rays come. These results were again checked in this work both on Mount Whitney and at Arrowhead Lake. One reading taken in a valley when the Milky Way was practically entirely behind the hills was not at all lower than when the Milky Way was overhead. *Within the limits of our uncertainty of measurement, then, these rays shoot through space equally in all directions.*

IV. Method of Obtaining Absorption Coefficients

In making the foregoing analysis for absorption coefficients the rays were assumed, for the reasons just given, to enter the atmosphere equally from all directions. Then the differential equation for the intensity I at a distance H beneath the surface, in terms of the intensity I_0 coming into the atmosphere from all directions outside its upper surface is

$$dI = 2\pi I_0 \sin\theta d\theta e^{-\mu H \sec\theta} \tag{1}$$

Therefore

$$I/I_0 = 2\pi \int_0^{\pi/2} \sin\theta e^{-\mu H \sec\theta} d\theta. \tag{2}$$

Putting $x = \sec\theta$ this takes the form

$$I/I_0 = 2\pi \int_1^{\infty} \frac{1}{x^2} e^{-\mu H x} dx. \tag{3}$$

Now Gold[7] has published a table of values of an integral of the type in Eq. (3) so that from this table it was possible to obtain the absorption coefficients of rays coming in from all directions. The method of doing this was to select the most reliable observed value near the top of each curve and to see what value of μ in the Gold table best reproduced the portion of the curve near it.

As stated above, however, *no one coefficient would fit the whole curve.* This result is completely new, we think, even as a suggestion, for heretofore it has been the uncertainty of measurement which has made the reported values of μ fluctuate from say .16 up to .57. Here, however, the variation from .18 up to .30 *represents the discrimination of measurement, rather than the uncertainty of reading.* Indeed, no previous observers had worked with the foregoing Gold law for the evaluation of μ since the uncertainty of measurement had theretofore made it useless to attempt to discriminate between rays following a linear absorption law and rays

[7] Gold, Proc. Roy. Soc. A82, 152 (1909).

coming in from all directions. The radiations have clearly become more penetrating with depth. In other words, the radiation is not homogeneous but consists of a spectrum of wave-lengths. For electroscope No. 3 the upper portion of the curve gave, as stated, $\mu = .30$ per meter of water, and the lower end $\mu = .18$. Electroscope No. 1 gave the same result for the lower end of the graph and a value slightly less for the upper end. Electroscope No. 3 was the more dependable since it had about double the sensitivity of No. 1. These coefficients of course characterize the radiation only throughout the region studied. Somewhat softer components are to be expected at greater altitudes.

V. Check Observations with Lead Screens

The same lead screens, 4.8 cm thick, used for making absorption experiments upon the radiations found about the granite rocks on top of Pikes Peak (see Part II) were taken to Muir Lake and observations similar to those there made repeated also upon granite rocks, both at Muir Lake (11,800 feet) and at Lone Pine (5500 feet). Then the instruments were brought back to Pasadena (759 feet) and similar observations made there on a soil consisting of decomposed granite. The lead was adapted for use with electroscope No. 1 alone and was the equivalent in absorbing power of 55 cm of water. The results of all these absorption experiments are collected in Table II.

Table II

Cosmic rays inside 4.8 cm lead

	Pasadena altitude 305 m	Lone Pine altitude 1676 m	Muir Lake altitude 3590 m	Pikes Peak altitude 4298 m
Ions per cc per sec. unshielded	13.0	16.7	20.0	23.7
Shielded with 4.8 cm Pb	9.0	10.1	11.8	12.6
External radiations after screening	1.6	2.7	4.4	5.2
Cosmic rays (theoretical)	1.3	2.4	4.1	4.9
Cosmic rays (observed)	1.32	2.21	4.08	5.0

In the first and second rows are given the readings without and with the lead shield, respectively. The figures in the third row are obtained by subtracting from those in the second row 7.4, which is seen from Fig. 3 to be the residual ionization in electroscope No. 1 when it is screened from all external radiation by being sunk to a depth of more than 50 feet in water. The third row, therefore, gives the total radiations of all kinds which penetrate at the various altitudes inside the lead screen.

A part of this radiation which gets through the lead is certainly due to the radioactive constituents of the surrounding rocks. Since these rocks were as nearly the same as possible in all the localities, a large variation

in the effect due to them is not to be expected. Kovarik and McKeehan[8] give the ionization on the earth due to γ rays from igneous rocks as about 3 ions. We have therefore taken 3 ions as a probable mean value of the ionization within the unshielded electroscope due to the gamma ray activity of the rocks. About 10 percent of this is able to get through a screen of water 55 cm thick. The figures in the fourth row are therefore obtained by subtracting .3 ions from those in the third row, and what is left, if the assumption as to the constancy of the radioactivity of the rocks is correct, should be, theoretically, the amount of the cosmic rays (see fourth row labelled "cosmic rays (theoretical)" which get through the lead screen in the various localities.

But now we have the possibility of getting these values in another and quite independent way, namely, by taking the readings on the curve of Fig. 3 at each location, for this gives how much of the cosmic radiation actually is present at each elevation, all soft radiations having been screened out by the water. It is then easy to calculate how much of this cosmic radiation will penetrate 55 cm of water, using the coefficient .3 per meter of water (as we compute from our curve the absorption coefficient of the cosmic rays at this depth to be) and the formula $I=I_0e^{-\mu d}$. This should be the correct formula for this case, since here the shield completely surrounds the electroscope, and most of the radiation goes through it practically perpendicularly. The results are shown in the last row and are labeled "cosmic rays (observed)." The agreement between the observed and computed values in the fourth and fifth rows, respectively, is excellent and shows that after working out the characteristics of the cosmic rays from the observations in water we can actually compute accurately the amount of these cosmic rays which will be found inside a 4.8 cm lead screen with the aid of the assumption that the only other rays which get through the lead screen are the rays from the radioactive constituents found in granite rocks.

VI. Soft Secondary (?) Rays

The agreement in Table II between the cosmic rays actually observed inside the lead (row 5) and those computed (row 4) on the assumption that the only other rays which can get inside the lead are the gamma rays due to the radioactivity of the granite rocks, assumed to be everywhere the same and equal to 3 ions, is apparently good evidence that the considerable amount of other soft radiations of local origin observed by Millikan and Otis on Pikes Peak is unable to penetrate appreciably 4.8

[8] Kovarik and McKeehan, Report of Committee on X-rays and Radioactivity, National Research Council, Washington, D. C., p. 141 (1925).

cm of lead. Before drawing inferences as to the nature and origin of these new soft rays, Table III is presented to show again their existence and distribution with altitude. The first row of this table repeats the total observed ionization inside the unshielded electroscope in the indicated localities, the second row the readings from the cosmic ray curve, Fig. 3. The differences between these two are found in the third row and represent all the rays which have passed through the walls of the unshielded electroscope No. 1 except the cosmic rays, i.e., all the rays of local origin which enter the electroscope from without.

Table III

Soft secondary radiation

	Pasadena 305 m	Lone Pine 1676 m	Muir Lake 3590 m	Pikes Peak 4298 m
Direct observation	13.0	16.7	20.0	23.7
Cosmic rays (from curve)	8.95	10.0	12.2	13.3
Soft rays (observed)	4.05	6.7	7.8	10.4
Stimulated soft rays (assumed)	1.05	3.7	4.8	7.4
Stimulating cosmic rays (observed)	1.55	2.6	4.8	5.9

Since we have just assumed the radioactive rays from the granite rocks to be responsible for 3 of these observed ions per cc per sec., the difference given in the fourth row represents other soft local rays. However, any error in the assumption of the uniform value 3 for the gamma rays of local origin would vitiate badly the fourth row of Table III, whereas it would have had but a small influence on the fourth row of Table II. The reason for this is that the total effect of these gamma rays inside the lead (fourth row, Table II) is but a few tenths of an ion at most, while in the fourth row of Table III it is ten times as much. The fifth row of Table III gives the actual values of the cosmic rays found within the unshielded electroscope. These are obtained from curve 4 for the various altitudes by subtracting the residual ionization, 7.4 ions, from the curve reading. It will be seen that there is a rough proportionality between the stimulating cosmic rays found in row 5 and the new soft rays shown in row 4. This is perhaps sufficiently good, in view of the aforementioned cause of uncertainty as to the values in the fourth row, to furnish evidence that the new soft rays of the fourth row are produced by the cosmic rays of row 5. Row 4 is therefore labeled "Stimulated soft rays." The argument here, however, is not one of certainty. The observed increase with altitude of the soft rays might be explained by making the unlikely assumption that quite accidentally we were observing on rocks of increasing gamma radiation as we progressed upward. Further experiments are needed to settle this point unambiguously.

VII. The Spectral Distribution of the Observed Cosmic Rays

In order to obtain the spectral distribution of rays such as those here found for which the absorption coefficients are as low as 1/20 of those of RaC or ThD and vary from .3 per meter of water to .18 per meter of water there is as yet no altogether infallible guide. But the very recent experimental work of Ahmad[9] has shown that the gamma rays of radium in their absorption by matter obey the same general law as x-rays, and for these the relation between absorption coefficient and frequency is well known. Compton's theory of scattering predicts Ahmad's observational data very satisfactorily. According to the Compton-Ahmad formula the mass absorption coefficients may be calculated from the formula

$$\frac{\mu}{\rho}=\left\{\frac{\sigma_0}{1+2\alpha}+B\lambda^3Z^3\right\}\frac{ZN}{A} \tag{4}$$

the first term of which represents "Compton scattering" while the last is "true absorption" (ejection of photo-electrons). For absorption in water this last term is nearly negligible even for gamma-ray wave-lengths, so that it must certainly be negligible for the much harder rays here under consideration, so that for these rays

$$\frac{\mu}{\rho}=\left\{\frac{\sigma_0}{1+2\alpha}\right\}\frac{ZN}{A} \tag{5}$$

where

$$\alpha=\frac{.0242}{\lambda} \text{ and } \sigma_0=6.64\times10.^{-25} \tag{6}$$

Making the substitution of $Z/A=10/18$, its value for water, $N=6.06\times10^{23}$ and the observed range of absorption coefficients, namely, .0030 and .0018 we obtain $\lambda=.000634$A and $\lambda=.00038$A, respectively, or a spectral range of a little less than an octave in a region of frequencies about 50 times higher than that of the shortest measured gamma rays ($\lambda=.02$A). The foregoing reduction of absorption coefficients to wave-length has been given very considerable credentials by Ahmad's experimental proof of the ability of the Compton theory to predict fairly closely his observed results.[10] Also very nearly the same wave-lengths are obtained from Dirac's relativity-quantum-mechanics formula.[11] This yields about 30 percent lower wave-length values.

[9] N. Ahmad, Proc. Roy. Soc. **109**, 206 (1925).

[10] A paper has just appeared by Hoffman, Phys. Zeits. **36**, 25 (1926) which lends further support to the reliability of Compton's equations for the purpose in question.

[11] Dirac, Proc. Roy. Soc. **111**, 405 (1926).

VIII. Nature of Soft Stimulated Radiations

We observe, first, that according to Compton's equations[12] the mean ratio of true scattering to true absorption—this is the ratio between the mean energy in the scattered quant and the energy in the recoil electron —is given by

$$\frac{\sigma_s}{\sigma_a} = \frac{1+\alpha}{\alpha} \tag{7}$$

Since, for the cosmic rays, λ is of the order .0005 the quantity α is large compared to unity and therefore for this case

$$\frac{\sigma_s}{\sigma_a} = 1 \tag{8}$$

This means that on the average each particular act of scattering divides the energy of the original quant equally between the new quant and the recoil electron, and the scattered quant has therefore on the average twice the wave-length, or half the frequency of the original one.

Also, according to Compton's equations the average angle of scattering is given by

$$\lambda - \lambda_0 = .0242(1-\cos\theta)$$

and since for the cosmic ray, as just shown, $\lambda = 2\lambda_0$ we have

$$(1-\cos\theta) = .0005/.024 = .02$$

$$\cos\theta = .98 \text{ or } \theta = 11°$$

Further, since the original momentum in the direction of the ray is $h\nu_0/c$ and the momentum remaining in the scattered quant, namely $h\nu_0/c$ is very nearly $h\nu_0/2c$, since θ is small, it follows that the momentum imparted to the recoil electron in the direction of the original ray must also be exceedingly close to $h\nu_0/2c$. In other words, *the act of scattering of these very high frequency rays consists merely in taking half the energy of the light quant and transferring it to a recoil electron, both this new light-quant and the electron moving practically straight forward in the direction of the original beam, each with half the original energy.*

Altogether without reference to Compton's theory, the fact that the electrons do actually move more and more nearly straight forward as the frequency of the ray increases is shown directly by the C. T. R. Wilson photographs, so that the qualitative correctness of the foregoing conclusion can scarcely be doubted.

The foregoing equations show that contrary to Eddington's assumption[13] very high frequency cosmic rays do not degenerate in one scattering

[12] A. H. Compton, Phys. Rev. 21, 494 (1923).
[13] Eddington, Nature 117, 31 (1926).

act into rays of gamma-ray frequency as they would if, on the average θ were 90°, but instead, since θ is always very small, they soften to just one-half frequency at each act. Since further, in the process of the degeneration, the energy left in the ether-wave is always proportional to its frequency, when a cosmic ray of wave-length $\lambda = .0005$A has degenerated to an ordinary gamma-ray of wave-length $\lambda = .025$ it has left in it but 1/50th of the original energy. This shows, for example, *that if at a given altitude the cosmic rays produce say 5 ions per cc per sec. there is a wholly negligible ethereal radiation of gamma ray hardness mixed with them.* Indeed, until the radiation has become pretty well absorbed (reduced to less than half its original energy) the bulk of the ionization is due to the primary rays, a smaller part to the secondaries (of half the original frequency) a smaller part still to the tertiaries (of one-fourth the original frequency), and a very small part to all the other members of the series. In other words, while cosmic rays diminish in energy as they go through matter because some of the quanta are removed from the beam by scattering, they soften, or diminish in frequency, very little before the intensity of the beam has been reduced to a small fraction of the original value. Even then it is the secondaries and tertiaries which carry the bulk of the energy, so that the beam has not, on the average, degenerated to anything like gamma-ray hardness. Indeed, a more complete analysis on the basis of the Compton equation shows that *no matter how much the intensity of an originally monochromatic beam has been reduced by passage through matter, of whatever thickness, more than three-fourths of the resultant ether-wave energy is carried by the primaries, secondaries, and tertiaries whose frequencies are respectively 1, 1/2 and 1/4 times the original frequency.* We cannot, therefore, seek the source of the rays "of gamma-ray hardness" found on Pikes Peak in cosmic rays degenerated into actual gamma-rays by Compton scattering.

On the other hand, the following analysis shows that the observed soft rays are in part, at least, the β rays produced by the cosmic rays. For one-half of the incident energy in each cosmic ray goes over in each scattering act into the recoil electron. The highest frequency cosmic ray observed ($\lambda = .00038$) has an energy-value corresponding to the fall of an electron through about 30,000,000 volts. Hence the beta-rays produced by the impact of these with electrons in Compton scattering have an energy of about 15,000,000 volts. The velocity of a 7,500,000 volt beta-ray, in terms of the velocity of light, is .998,[14] and since volts vary as $1/1-\theta^2$, which is proportional, for $\beta \doteq 1$, to $1/\sqrt{2(1-\beta)}$ for 15,000,000 volts rays $\beta = .9995$.

[14] National Research Council, Bulletin on Radioactivity, p. 92 (1925).

Now Bohr[15] has worked out the average range of β-rays as given in Table IV, finding the range proportional to $1/\sqrt{1-\beta^2}$ and Varder[16] has given Bohr's formula experimental verification. It will be seen from the formula and the table that for large velocities the range is proportional to the energy.

TABLE IV

Showing variation of average range with velocity

Velocity of corpuscle / Velocity of light	Average range meters
0.80	0.7
0.85	1.1
0.90	1.9
0.95	3.5
0.99	10.5
0.996	18.0
0.998	26.0
0.9995	52.0

We see, therefore, that beta rays having a range of 52 m in air, equivalent to 5.1 mm of brass, are produced by each act of scattering of the initial cosmic rays. *These are undoubtedly a part, at least, of the soft rays found on Pikes Peak.* In a preceding communication[17] these have been referred to merely as "rays of about gamma-ray hardness," not as actual gamma-rays, though various authors have so understood them.

IX. ORIGIN OF THE COSMIC RAY

It is altogether obvious that any rays of the hardness and distribution indicated, and of cosmic origin, must arise from nuclear changes of some sort going on all about the earth. The energy of the change involved is, however, four times that of any radioactive change thus far on record, being equivalent, for rays of wave-length $\lambda = .00038$ to the fall of an electron through a potential difference of 32,400,000 volts, and for rays of wave-length $\lambda = .000634$ to 19,500,000 volts. The fastest β-ray on record has an energy of 7,500,000 volts.

Both Eddington[18] and Jeans[19] wish to regard these observed cosmic rays as arising from the transmutation of the mass of the proton into radiation by the union of a proton with a negative electron. They regard this process as going on both in the nebulae and in the interior of stars. Such a process, however, would produce a ray of wave-length .000013A, which would be thirty times more energetic and more penetrating than the shortest wave-length which we have observed. This hypothesis does not seem to be tenable if the Compton equations are to be taken as guides,

[15] N. Bohr, Phil. Mag. **30**, 518 (1915).
[16] Varder, Phil. Mag. **29**, 731 (1915).
[17] Millikan, Proc. Natl. Acad. Sci., January (1926).
[18] Eddington, Nature **117**, 26 (1926).
[19] Jeans, Nature **116**, 861 (1925).

for, as already indicated, rays having that energy could not be softened to an average one-thirtieth of their original frequency by passage through any amount of matter. Their energy could all be dissipated in heat through the beta-rays, but such radiation as got out undissipated would have a considerable fraction of its energy in the original frequency.

Again, if rays thirty times the hardness of the rays observed were present we should not have found in two lakes our electroscopes reaching a constancy of reading at all depths below fifty feet. The reasons adduced by Eddington for assuming that this process is going on seem good, but its seat, if it exists, is presumably in the interiors of stars alone where the energy of the change is all frittered away into heat, through the medium of the beta-rays, before any appreciable part of it has found its way out into space. *The cosmic rays are probably, therefore, not degenerated waves of higher frequency, but are rather generated by nuclear changes having energy values not far from those recorded above.* These changes may be (1) the capture of an electron by the nucleus of a light atom, (2) the formation of helium out of hydrogen, or (3) some new type of nuclear change, such as the condensation of radiation into atoms. The changes are presumably going on not in the stars but in the nebulous matter in space, i.e., throughout the depths of the universe.

Summary

The advances made in these researches seem to us to be

(1) The increased precision, definiteness, and unambiguity with which the properties of the penetrating rays have been brought to light.

(2) The definite proof that some of these rays come from above, the 6700 feet of atmosphere between 11,800 and 5,100 acting merely as a blanket equivalent to six feet of water. This is by far the best evidence found so far for the view that the penetrating rays are partially of cosmic origin.

(3) The bringing forth of evidence for the spectral distribution of cosmic rays and the rough determination of the frequency limits of the spectrum. This is altogether new.

(4) The bringing forth of evidence for the existence of a secondary very penetrating beta radiation stimulated by the primary cosmic rays.

(5) The fixing of the ionization at the earth's surface due to cosmic rays, as measured inside electroscope No. 1 at about 1.4 ions.

The whole of this cosmic ray work has been done with the aid of funds provided by the Carnegie Corporation of New York and administered by the Carnegie Institution of Washington.

Norman Bridge Laboratory of Physics,
California Institute of Technology, Pasadena.
August 7, 1926.

THE INTENSITY OF REFLECTION OF X-RAYS BY POWDERED CRYSTALS, I. SODIUM CHLORIDE AND SODIUM, LITHIUM AND CALCIUM FLUORIDES.*

By R. J. Havighurst**

Abstract

Through measurements by the ionization method of the relative intensities of reflection of x-rays by the different planes of *powdered crystals*, the author has obtained data which are free from the errors inherent in the work with large single crystals. Darwin's formula for the intensity of reflection from an ideally imperfect crystal may be applied to these results without correction for primary or secondary extinction. In order to get reflected radiation of sufficient intensity to permit accurate measurement, a focussing method has been used, in which a primary beam of wide divergence strikes the surface of a briquet of the powder under investigation and the reflected beam is focussed sharply at the ionization chamber slit. Measurements were made out to angles slightly larger than $\theta=45°$. The absolute values of the intensity of reflection were determined by comparison with reflections from powdered sodium chloride, the results of Bragg, James and Bosanquet on the latter crystal, after allowance for secondary extinction, being taken as correct.

Structure factor and atomic scattering curves.—Application of the equation for the intensity of x-ray reflection to the experimental results gives the structure factors for the reflections from the different crystals. These factors, when plotted against $\sin\theta$, fall upon smooth curves from which can be obtained the atomic scattering curves representing the variation of the atomic structure factors with the angle of reflection. For fluorine in all three fluorides, the F curves are almost identical, but for sodium in NaF and NaCl there is a notable difference, indicating that the electron distribution for Na is not the same in the two compounds. The effect of the excess positive or negative charge which tightens or loosens the electron atmosphere of an ion is made evident by comparison of the F curves for ions of different charge but with the same number of electrons. Use of experimental structure factor curves in crystal analysis is discussed.

Introduction

RECENTLY there has appeared a paper by W. L. Bragg, Darwin and James[1] which gives a comprehensive survey of theoretical and experimental work on the intensity of reflection of x-rays by crystals. Theoretical treatment of the problem gives rise to two different expressions for the intensity of reflection, depending upon certain assumptions as to the nature of the crystal. One of these expressions may be applied to the case of reflection by a perfect crystal; that is, one which

* A preliminary account of a part of this work has been published in Proc. Nat. Acad. Sci. 12, 380 (1926).

** National Research Fellow.

[1] W. L. Bragg, Darwin and James, Phil. Mag. 1, 897 (1926).

is a homogeneous unit, with each atomic plane strictly parallel to every corresponding atomic plane. The other expression applies to the case of an ideally imperfect crystal; that is, one which is composed of a *mosaic* of very small perfect crystal blocks that are only approximately parallel to each other. The most important difference between the two expressions is that the formula for the perfect crystal makes the intensity of reflection proportional to the first power of the structure amplitude, while the formula for the imperfect crystal, on the other hand, makes the intensity proportional to the square of the structure amplitude. Through experimental tests on various crystals, it has been found that most of them are of the imperfect rather than of the perfect type, but their perfection is nevertheless sufficiently high to make it necessary to modify the mosaic formula. The modification takes the form of a correction for *primary extinction* in the crystal, which can be evaluated only indirectly. The nature of extinction and the manner of determining and applying the correction have been fully discussed by these authors, and we shall base the text of this paper on the assumption that the reader is familiar with the status of the problem as presented by them.

The writer has been working on the problem of the intensity of x-ray reflection from a somewhat different angle, which seems to offer a direct means of determining the scattering power—that is, the effect of extinction is mechanically eliminated and the formula for the ideally imperfect crystal applies strictly to the measurements. Preliminary accounts of this work have been published,[2] giving the conclusions of the author in regard to the nature of crystals and the amount of extinction to be met in measurements on single crystals which are in general agreement with the ideas of Bragg, Darwin and James.

The method used by the author consists of the measurement of the intensity of x-ray reflection from powdered crystals. When the individual crystal particles become as small as 10^{-2}–10^{-3} cm in size, secondary extinction becomes negligible; it may be dismissed from consideration in measurements by the powder method. Primary extinction, on the other hand, remains effective until the size of the perfect crystal blocks in the powder is as small as 5×10^{-5} cm. The size of the particles of a powder ground mechanically is usually larger than 10^{-5} cm, hence if the powder particles are perfect crystals, primary extinction would still be present. In an investigation of primary extinction which is described in the following paper, the author has measured the reflections from powdered crystals of various particle sizes; these measurements indicate

[2] Havighurst, Proc. Nat. Acad. Sci. **12**, 375, 380 (1926); Phys. Rev. **27**, 243 (1926).

that primary extinction is absent from a thoroughly ground powder of any of the substances to be considered here, so the perfect crystal blocks must be smaller than the powder particles themselves. We may anticipate this result then, and assume for the purposes of the present paper that extinction, both primary and ordinary, is entirely eliminated in measurements by the powdered crystal method.

Preliminary measurements have been made by Compton and Freeman[3] on powdered sodium chloride, and Darwin[4] has suggested that measurements by the powder method should give valuable information concerning extinction. The chief difficulty in the way of obtaining reliable intensity measurements by the powder method lies in getting enough radiation reflected from the planes reflecting at large angles for accurate measurement with an ionization chamber.

A brief description of the author's method of securing the necessary intensity will be followed by a survey of measurements upon sodium chloride and lithium, sodium and calcium fluorides. From these measurements the structure factor curves for the various classes of planes in the crystals and finally the atomic scattering curves for the atoms composing these crystals, are obtained.

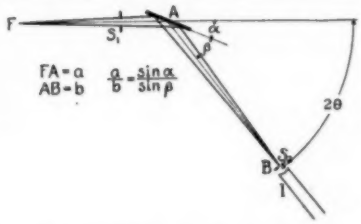

Fig. 1. Diagram illustrating focussing method.

Experimental

In Fig. 1 is shown a diagram of the experimental arrangement. Brentano[5] has described the focussing method, which is a generalization of the familiar Bragg "focussing condition." For reflection from the face of a briquet of powder, A, mounted at the center of an ionization spectrometer, the distances from focal spot to powder, a, and from powder to ionization chamber, b, determine the ratio $a/b = \sin\alpha/\sin\beta$, where α is the angle between the primary beam and the surface of the briquet, and $\beta = 2\theta - \alpha$. When this condition is fulfilled the reflected radiation is focussed at the ionization chamber slit to a beam of the same width as that of the primary beam issuing from the focal spot. By means of the auxiliary slit S_1, the divergence of the primary beam may be regulated so that a reflected beam of the desired intensity is obtained; at small angles of reflection, S_1 is rather narrow, but for the measurement of reflections at large angles, S_1 is widened until the divergence of the primary beam is

[3] A. H. Compton and N. L. Freeman, Nature **110**, 38 (1922).
[4] Darwin, Phil. Mag. **43**, 800 (1922).
[5] Brentano, Proc. Phys. Soc. London **37**, 184 (1925).

5 to 6°. Measurements are made over groups of reflections which do not differ too greatly in intensity, the only precaution beyond the fulfillment of the focussing condition being that the surface of the briquet shall intercept the whole of the primary beam in every case. With the apparatus in use by the author, reflections were measured out to angles slightly larger than $\theta = 45°$.

The primary beam from a Mo tube was rendered nearly monochromatic by filtration through enough ZrO_2 to reduce Mo $K(\gamma+\beta)$ to less than 0.4 percent of Mo $K(\alpha_1+\alpha_2)$, while the maximum height of the general radiation curve corresponded to an intensity of about 0.3 percent of the α peak at $\lambda = .710$A. Only in two or three cases where the β peak from a strongly reflecting set of planes fell in the neighborhood of a very weak α reflection was it necessary to take into consideration the existence of the β peak. The x-ray tube was operated by a high potential storage battery[6] at 35000 volts and about 25 milliamperes.

Relative intensities could be measured with an error of less than 5 percent except in the case of very weak reflections. The ionization chamber was moved through the width of the slit at each reading and the sum of the ionization currents, after application of a base-line correction, was taken as a measure of the intensity of reflection. Various slit widths were used, including some wide enough to take in the whole reflected beam, with concordant results. The chief source of error lay probably in the base-line correction, since the reflection on the long wave-length side of a peak is always slightly larger than that on the short wave-length side in the case of filtered Mo radiation. However, a standard method of drawing the base-line was adopted, and should be quite satisfactory in the measurement of relative intensities, the only kind of measurements which the author has made. The conceivable sources of systematic error have been investigated. It was found that the pressure used in making the briquet had a tendency to orient the surface layer of crystals if they were larger than 10^{-3} cm in size. Consequently, the original surface of each briquet was shaved off.

As a check on the measurements by surface reflection, and also in the measurements (to be described below) of the relative intensity of reflection by different substances, the method of measuring the intensity of the radiation reflected by and transmitted through a thin plate of powder was used. Because the primary beam must be narrow in this method, only the strongest reflections could be measured, but these

[6] Armstrong and Stifler, J. Optical Soc. Am. **11**, 509 (1925).

measurements agreed satisfactorily with those made by the surface reflection method.

Structure-Factor Determinations from Powder-Method Measurements

In his discussion of the intensity of x-ray reflection,[7] A. H. Compton sets forth the theory of reflection by a powder and derives the following formula for the intensity of reflection of x-rays from the surface of a thick briquet of powder:

$$\frac{P_s}{P}=\frac{jl}{16\pi r\mu\sin\theta}\times Q=\frac{jlN^2F^2\lambda^3}{64\pi r\mu}\,\frac{e^4}{m^2c^4}\,\frac{1+\cos^2 2\theta}{\sin^2\theta\cos\theta} \tag{1}$$

P is the power in the primary beam; P_s is the power in the scattered beam which is reflected into an ionization chamber distant r from the powder and having a slit height l which is small compared with $r \sin 2\theta$; j is the number of planes belonging to the crystal form which is reflecting the x-rays; the Q of Bragg, Darwin and James would take the form given above when actually used with experimental data; N is the number of molecules per cc and F^2 contains the Debye temperature factor, $e^{-(b^2 \sin^2\theta)/\lambda^2}$. It seems best to include the Debye factor in the structure factor F because of the difficulty in making a separate evaluation of it. Both factors depend upon $(\sin\theta)/\lambda$ and the arrangement of the electrons in the unit cell, and the inclusion of the Debye factor in F simply means that the structure factor now depends upon the time means of the positions of the electrons with respect to the stationary points of the crystal lattice, rather than upon their positions with respect to nuclei which, together with their electron atmospheres, are subject to the motions of thermal agitation.

Using the above expression it is possible to calculate the absolute value of F from a measurement of the intensity of reflection. But we are primarily interested in relative F values, and consequently may drop everything out of Eq. (1) which is independent of the angle of reflection. This leaves

$$F^2\propto\frac{P_s}{j}\,\frac{\sin^2\theta\cos\theta}{1+\cos^2 2\theta} \tag{2}$$

A single absolute F value for each substance will suffice to place on an absolute scale all of the results obtained by the use of expression (2).

[7] A. H. Compton, X-rays and Electrons, Chap. 5; Van Nostrand and Company (1926). The author wishes to thank Professor Compton for the privilege of using this material in manuscript form.

The author's method of determining absolute values of F depends upon a measurement of F for one or more planes of each substance relative to the F value of the NaCl (220) reflection. From the measurements of Bragg, James and Bosanquet[8] on single crystals of rock-salt, corrected for secondary extinction, we find $F(220)=15.75$. There is good reason to believe that this determination is unaffected by primary extinction, since the powder method measurements of relative intensity are in agreement with those of Bragg, James and Bosanquet when the latter are corrected for secondary extinction. Therefore all F determinations in this paper are based upon an absolute value of 15.75 for $F(220)$ of NaCl.

If we measure P_s for the (220) plane of NaCl and then, keeping the intensity of the primary beam constant, replace the briquet of NaCl with a briquet of another substance (X) and measure P_s for some set of planes in this substance, we get from Eq. (1)

$$F_X^2=\frac{P_{sX}}{P_{sNaCl(220)}}\left(\frac{j\,N^2F^2}{\mu}\,\frac{1+\cos^2 2\theta}{\sin^2\theta\cos\theta}\right)_{NaCl(220)}\left(\frac{\sin^2\theta\cos\theta}{1+\cos^2 2\theta}\,\frac{\mu}{jN^2}\right)_X \quad (3)$$

By a similar process we get, for the case of reflection through a thin plate of crystal powder which is always kept in such a position that the normal to its surface makes an angle θ with the incident beam,

$$F_X^2=\frac{P_{sX}}{P_{sNaCl(220)}}\,\frac{(h\sec\theta e^{-\mu h\sec\theta})_{NaCl(220)}}{(h\sec\theta e^{-\mu h\sec\theta})_X}\left(\frac{j\,N^2F^2(1+\cos^2 2\theta)}{\sin^2\theta\cos\theta}\right)_{NaCl(220)}\left(\frac{\sin^2\theta\cos\theta}{j\,N^2(1+\cos^2 2\theta)}\right)_X \quad (4)$$

h is the thickness of the crystal powder plate and μ is the linear absorption of the powder, the thickness being determined by the weight and surface area of the sample, so that the interstices between the powder particles do not cause error.

In some cases the author used both surface reflection and transmission methods, but the latter proved the more satisfactory. At least one reflection was evaluated for each of the fluorides of lithium, sodium, and calcium, the results being given in Table I.

With the aid of the F values of Table I, we can evaluate the data obtained by the application of expression (2) to the powder method measurements. In Tables IIA and IIB are given the F values for all the reflections which were measured, as well as the atomic F values for the separate atoms composing the crystal planes.

[8] W. L. Bragg, James and Bosanquet, Phil. Mag. 42, 1 (1921).

TABLE I

Absolute F values obtained by comparison with NaCl (220)

$$R_r = P_{sX}/P_{s\ NaCl(220)};\ R_t = \frac{P_{sX}(h \sec\theta \exp[-\mu h \sec\theta])_{NaCl(220)}}{P_{s\ NaCl(220)}(h \sec\theta \exp[-\mu h \sec\theta])_X}$$

Substance	Plane	N^2	μ	Reflection		Transmission	
				R_r	F	R_t	F
NaCl	200	5.02×10^{44}	17.45	1.73	20.60	1.75	20.70
	220			*1.00*	*15.75*	*1.00*	*15.75*
NaF	200	16.23	7.24	4.17	14.01	1.87	14.45
	220			2.30	10.54	1.00	10.87
LiF	220	37.62	4.59			0.34	4.80
CaF_2	111	6.10	36.2			2.18	16.06
	220					2.44	23.00

TABLE IIA

F values for sodium chloride and calcium fluoride

Plane	CaF_2				NaCl			
	$\sin\theta$	F	F_{Ca}	F_F	$\sin\theta$	F	F_{Na}	F_{Cl}
111	0.1124	15.90	15.90		0.109	4.55	9.00	13.60
200	.1298				.126	20.80	8.58	12.23
220	.1836	23.20		5.45	.178	15.75	6.55	9.20
311	.2153	11.16	11.16	4.25	.209	2.40	5.70	8.10
222	.2249				.218	13.30	5.46	7.84
400	.2597	16.42		3.26	.252	11.60	4.62	6.93
331	.2829	9.26	9.26	2.95	.275			
420	.2903				.282	10.20	3.97	6.21
422	.3180	13.30		2.56	.309	8.95	3.38	5.58
511, 333	.3373	7.32	7.32	2.43	.328	2.18	3.05	5.15
440	.3672	10.57		1.96	.357	7.18	2.55	4.64
531	.3841	*6.27*	6.27		.373			
600, 442	.3895	*2.24*			.378	6.69	2.23	4.25
620	.4105	9.20		1.63	.399	6.03	1.99	3.95
533	.4257	*5.65*	5.65		.414			
622	.4305	*1.71*			.418	5.62	1.80	3.67
444	.4497	8.23		1.56	.437			
640	.4681				.455	4.75	1.45	3.16
642	.4857	7.38		1.28	.472	4.10	1.27	2.88
553, 731	.4985	4.80	4.80		.485	1.56	1.15	2.72
800	.5193				.504	3.54	1.00	2.50
733	.5313	*4.37*	4.37		.516			
820, 644	.5353	*1.72*			.520	3.31	0.88	2.35
822, 660	.5508	6.06		0.97	.535	3.08	0.78	2.20
751, 555	.5621	*3.97*	3.97		.546			
662	.5659	*1.79*			.549			
840	.5805	5.53		0.90	.564	2.64	0.63	1.98
664	.6088	4.95		0.80	.590	2.23	0.42	1.70
931	.6192	3.20	3.20		.602	1.23	0.36	1.60
844	.6355				.617	1.75	0.29	1.47
862, 10 20	.6620	4.30		0.69	.642	1.54	0.20	1.35
953	.6962	*2.66*	2.66					
864, 10 40	.6990	*1.15*						
10 42	.7111	3.68		0.53				
775, 11 11	.7200	2.58	2.58					

TABLE IIB

F values for sodium fluoride and lithium fluoride

Plane	NaF sin θ	NaF F	NaF F_{Na}	NaF F_F	LiF sin θ	LiF F	LiF F_{Li}	LiF F_F
111	0.133	1.27			0.153	4.61	1.26	5.89
200	.154	14.25	7.76	6.49	.177	6.73	1.25	5.46
220	.217	10.80	6.15	4.65	.250	4.70	1.09	3.63
311	.255	1.38		3.73	.293	1.96	2.91	0.95
222	.266	8.39	4.90	3.49	.306	3.70	2.78	0.92
400	.307	6.59	4.03	2.56	.354	2.64	2.12	0.53
331	.335	1.46		2.13	.386	1.34	1.87	0.53
420	.344	5.51	3.44	2.07	.396	2.31	1.78	0.53
422	.377	4.75	2.99	1.76	.433	1.93	1.47	0.46
511, 333	.399	1.06	2.65	1.59	.460	0.89	1.30	0.41
440	.435	3.46	2.09	1.37	.501	1.37	1.06	0.31
531	.455	0.63		1.23	.524			
600, 442	.461	3.04			.531			
620	.486	2.55			.560	0.96	0.79	0.17
533	.504				.580	0.58		
622	.510	2.38	1.40	0.98	.587	0.87		
711, 551	.550				.632	0.47		
640	.554				.638	0.73		
642	.575	1.86			.662	0.70	0.57	0.13
553, 731	.590	0.39	1.06	0.67	.680	0.41	0.53	0.12
733	.629				.724	0.35		
820, 644	.634	1.41			.730	0.53	0.45	0.08
822, 660	.652	1.33	0.78	0.55				
840	.688	1.22						
842	.705	1.03						
664	.721	0.92						
931	.733	0.00	0.43	0.43				

STRUCTURE-FACTOR CURVES

In Figs. 2–5 the F values for the crystal planes are plotted against $\sin\theta$. The resulting curves are generally smooth, but show certain definite irregularities which will be discussed later.

Sodium chloride. The curves agree with those of Bragg, James and Bosanquet when the latter are corrected for secondary extinction. The extent of the agreement is shown in Fig. 2, where the author's data are represented by circles, and those of Bragg, James and Bosanquet by crosses.

Lithium fluoride. Since a small amount of heavy impurity in solid solution would cause a considerable change in the scattering power of LiF, the sample was carefully freed from Ca and Mg and several times reprecipitated. The upper curve of Fig. 3 represents planes with all even indices, in which Li and F re-enforce each other; in the lower curve,

for planes with all odd indices, Li interferes with F. Debye and Scherrer[9] have determined the relative intensities of reflection from the first nine planes of LiF by a photometric study of powder method photographs. Their results fall reasonably well upon the curves of Fig. 3. They interpreted their work as proof that the crystal lattice consists of Li^+ and F^-

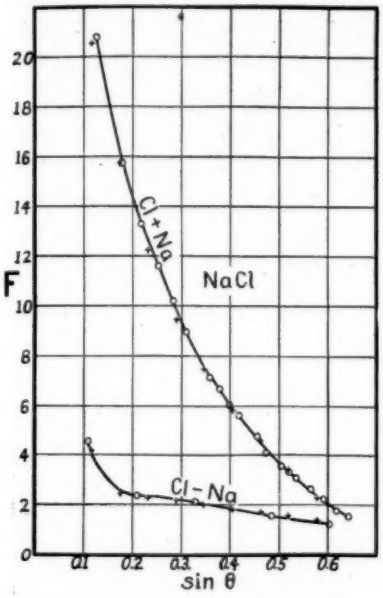

Fig. 2. Structure factor curves for sodium chloride.

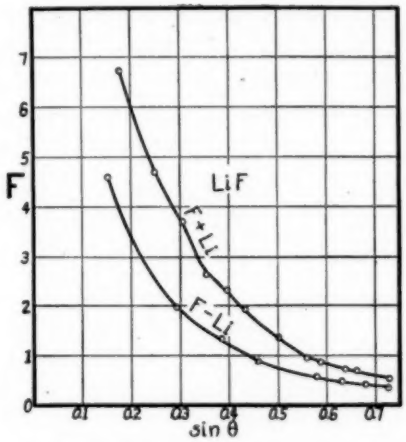

Fig. 3. Structure factor curves for lithium fluoride.

ions, rather than of neutral atoms. We know that the F values should be equal to the number of electrons in the atoms composing the crystal planes at zero angle of reflection. Consequently the F+Li curve should approach the value 12, and the F−Li curve should approach the value 8 if the lattice consists of ions, or 6 if the lattice consists of neutral atoms. The corresponding ratios of (F+Li)/(F−Li) are 1.5 and 2. Debye and Scherrer, by extrapolating the curve representing this ratio to zero angle of reflection, obtained a value of approximately 1.5. While there is abundant evidence from other sources that the lattice of the alkali halides is ionic, the shape of the F curves at small angles is entirely unknown to us and reliance can hardly be placed upon curves extrapolated into this region. The ratio (F+Li)/(F−Li) in Fig. 3 varies between 2 and 1.5, and seems to be approaching the smaller value at small angles.

It is interesting, in connection with recent investigations of the Compton effect in lithium, to observe that the regularly scattered radiation from Li in LiF has not fallen to zero at $\theta=45°$, corresponding to a

[9] Debye and Scherrer, Physik. Zeits. 19, 474 (1918).

scattering angle of 90°. It seems probable then, that there is still some unmodified radiation scattered by atomic lithium at 90°.

Sodium fluoride. Samples from two different sources, each sample containing about 99 percent NaF, were investigated, with resu'ts which were in satisfactory agreement. The curve labelled Na–F is of particular interest because it represents the difference in scattering power of the Na^+ and F^- ions, on the assumption that the lattice is ionic. This curve should pass through zero at $\sin\theta=0$. Since the ions have the same number of electrons, there seems at first no reason for assigning to Na^+ the larger scattering power. But Na^+, possessing a nuclear charge of +11, would bind its electrons more tightly than F^-, with a nuclear charge of +9. A system with electrons nearer its center has a larger scattering power through the angular domain covered by the curves of Fig. 4.

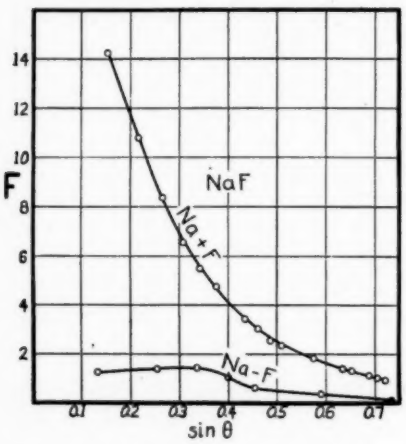

Fig. 4. Structure factor curves for sodium fluoride.

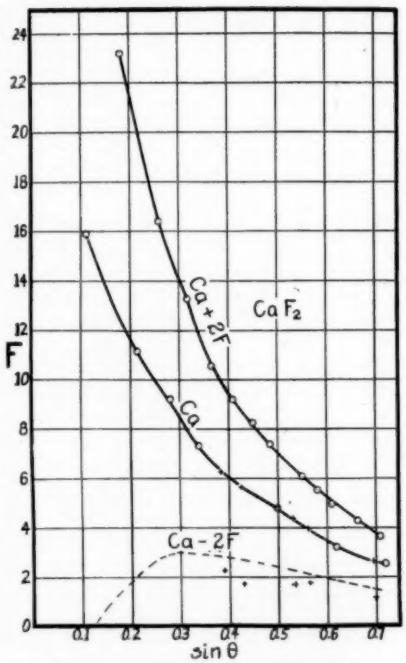

Fig. 5. Structure factor curves for calcium fluoride.

Calcium fluoride. Samples of ground fluorite, and a precipitated product containing less than half of one percent impurity, gave similar results. Fluorite, with a crystal structure different from that of the alkali halides, gives reflections which fall into three classes, as shown in the figure. The Ca–2F reflections are very weak, and occur so close to the Ca reflections that their measurement by the powder method is quite difficult; the points marked + on the two lower curves were obtained by an indirect method as follows: the combined intensity of a Ca reflection and its neighboring Ca–2F reflection was measured, an inter-

polated value from the Ca curve was used for the intensity of the Ca reflection and the amount left over from the total was assigned to the Ca–2F reflection. These values, which are italicized in Table IIA, are therefore only approximate. The broken line curve is that obtained for Ca–2F from the two upper curves. If the Ca^{++} ion, with eighteen electrons, is assumed to be present in the lattice together with two F^- ions, with 10 electrons apiece, the curve representing Ca–2F must drop to zero and rise again as a 2F–Ca curve to a value of 2 when $\sin\theta=0$. Here we see that Ca^{++}, with an excess positive charge, has drawn its electrons in and consequently scatters x-rays more strongly than the two F^- ions, which possess excess of negative charge.

Atomic Scattering Curves

In Figs. 6 and 7 are the atomic scattering curves obtained from the data of Tables IIA and IIB. Of particular interest is a comparison of the curves for the same ion in different compounds. It will be observed

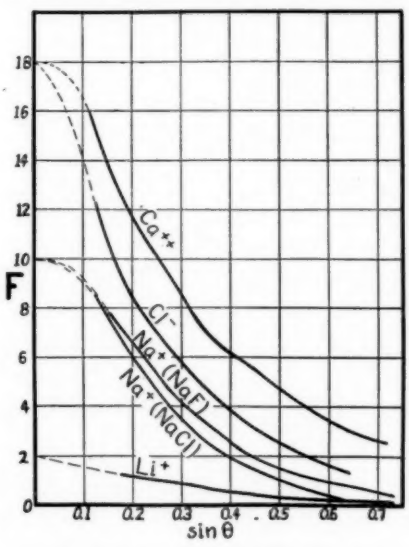

Fig. 6. Atomic scattering (structure factor) curves for various atoms.

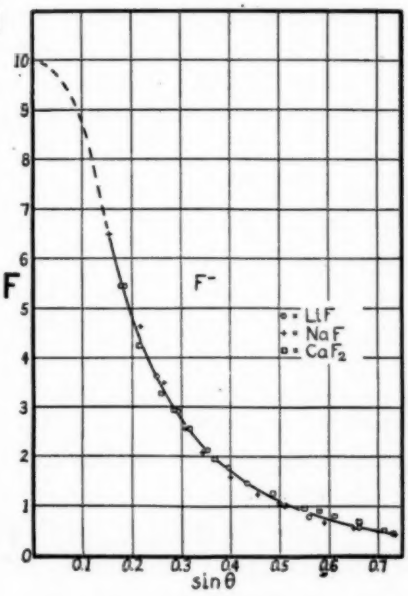

Fig. 7. Atomic scattering (structure factor) curve for fluorine.

that the Na curves from NaF and NaCl are considerably different, probably because of a difference in chemical, thermal, and crystal lattice forces in the two compounds. These forces have in NaF produced a marked tightening of the electron atmosphere of Na. On the other hand, the curves for fluorine from the different compounds are nearly alike. The

conclusion must be that the fluorine ion is in a force field of approximately the same magnitude in all three crystals. The curves for the atoms in fluorite are not in entire agreement with those of James and Randall,[10] because their correction for the extinction operative in their single crystal measurements does not make their results coincide with the author's powder method measurements.

Discussion of Results

Upon the basis of reliable atomic scattering curves may rest two very important results. In the first place, we may obtain direct evidence concerning the distribution of electrons in atoms. The author has worked out the electron distributions in all of the atoms considered here by means of a Fourier analysis based upon the data of this paper, and a description of this work will be published soon. In the second place, atomic scattering curves are an aid in the analysis of crystal structure. With a knowledge of the scattering curves of the atoms in a crystal, the structure factor for any atomic arrangement may be calculated and a quantitative analysis of the crystal structure can be made, provided the intensities of reflection are measured by the powder method or corrected satisfactorily so that the formula for the mosaic crystal holds strictly.

There is one serious error which may arise in an analysis of crystal structure made by this method. The atomic scattering curves may be appreciably different for the same atom in different chemical compounds, as in the case of Na from NaF and NaCl. In such a case it would be impossible to predict the scattering curve in the crystal under consideration. A discussion of the determination of parameters in crystal structure by the use of atomic scattering curves, as well as a description of another method of determining parameters which does not depend upon atomic scattering curves but involves a Fourier analysis making use of experimental measurements on the intensity of x-ray reflection, has recently been published.[11]

A study of the ratios of the ordinates of the atomic scattering curves for different values of $\sin\theta$ shows clearly that the assignment of scattering power to atoms in accordance with their total number of electrons is only a crude approximation. A similar variation of scattering power with angle of scattering is predicated by such a procedure. Especially erroneous is this assignment of scattering power in the case of oppositely charged ions (the usual case in crystal analysis) because the excess positive or negative charge produces a tightening or loosening of the elec-

[10] James and Randall, Phil. Mag. **1**, 1202 (1926).
[11] Havighurst, J. Am. Chem. Soc. **48**, 2113 (1926).

tron atmosphere of the original atom which profoundly affects its scattering properties.

The irregularities which are to be observed in the experimental curves may be due not so much to experimental error as to an actual difference of intensity of reflection by a crystal in different directions; that is, the electron distributions of the atoms may not be spherically symmetrical about the nuclei. It is very probable that in many crystals the atoms do not possess spherical symmetry, although the nearest approach to this condition would be expected in atoms belonging to crystals having a high cubic symmetry. At present there are no experimental measurements of sufficient accuracy to decide the question. Irregularities of a more smooth type would be expected from atoms in which there are definite shell-like structures of electrons and the gradual changes of slope due to such irregularities may exist in the experimental curves.

In conclusion the author wishes to express his gratitude to Professor William Duane for his advice and interest in this work.

JEFFERSON PHYSICAL LABORATORY,
HARVARD UNIVERSITY,
July 19, 1926.

THE INTENSITY OF REFLECTION OF X-RAYS BY POWDERED CRYSTALS. II. THE EFFECT OF CRYSTAL SIZE*

By R. J. Havighurst**

Abstract

The problem of *extinction* in its relation to the intensity of reflection of x-rays is studied by a comparison of measurements upon large single crystals with those upon powdered crystals of various particle sizes. The apparatus and method of making the measurements upon powders have been described in the preceding paper. Secondary extinction was not operative in the powder method measurements. Primary extinction is also absent in measurements upon thoroughly ground crystals of substances which, like the alkali halides, naturally form rather imperfect crystals; but a small amount of primary extinction may be produced by heat treatment of the powder. The relative intensities of reflection from the different planes of powdered NaCl, CaF_2 and calcite are compared with similar data from single crystal measurements on these substances. In the case of rock-salt, it is found that the single crystal measurements of Bragg, James and Bosanquet, when corrected for secondary extinction, agree with the powder method results, hence primary extinction was not operative in their experiments. The empirical correction for secondary extinction applied by James and Randall to their single crystal measurements upon CaF_2 is not quite large enough to produce agreement with the powder method data. Although the powder method measurements upon calcite, when comparedwith single crystal data, show that the latter have been affected by a great deal of extinction, it is not certain that a small amount of primary extinction was not operative even in the powder method measurements, for calcite forms very perfect crystals.

Introduction

THE importance of obtaining accurate measurements of the intensity of reflection of x-rays from crystals and the difficulty of interpreting the measurements after they have been obtained have been mentioned in the preceding paper and discussed fully in a paper by W. L. Bragg, Darwin and James.[1] In brief, the difficulty is this—there are two formulas for the intensity of x-ray reflection, one for the case of reflection by an absolutely perfect crystal, the other applying to an ideally imperfect crystal; measurements upon single crystals indicate that in some cases neither the conditions of absolute perfection nor those of absolute imperfection are actually satisfied, and consequently one of the formulas

* A preliminary account of part of this work has been published in Proc. Nat. Acad. Sci. 12, 375 (1926).

** National Research Fellow.

[1] W. L. Bragg, Darwin and James, Phil. Mag. 1, 897 (1926).

must be used (the one for an imperfect crystal) with a correction for the partial perfection of the crystal. Furthermore, there is no satisfactory method for the complete evaluation of this correction.

It is the author's purpose in this paper to prove that at least some crystalline substances when ground to fine powders become ideally imperfect crystals, and the corresponding formula may be applied without correction to measurements of the intensity of x-ray reflection by the powder method.

Darwin's formula[2] for the "integrated reflection," ρ, from a large ideally imperfect single crystal (one composed of a mosaic of very small blocks which are only approximately parallel to each other) is

$$\rho=\frac{N^2e^4}{m^2c^4}\,\frac{F^2\lambda^3}{2\mu}\,\frac{1+\cos^2 2\theta}{\sin 2\theta}=\frac{A^2}{2\mu}\,\frac{1+\cos^2 2\theta}{\sin 2\theta}=\frac{Q}{2\mu} \tag{1}$$

where N is the number of molecules per cc and the Debye temperature factor is included in F^2. Certain modifications of this formula which must be made before it can be applied to single crystal measurements take the form of corrections for *primary* and *secondary extinction*. Secondary extinction takes place only in imperfect crystals and represents a decrease in the intensity of reflection due to shielding of the blocks deep within a crystal by the reflection of the x-rays from the blocks near the surface. Single crystal measurements may be corrected satisfactorily for secondary extinction. It is proportional to the intensity of reflection and causes an effect of the same order of magnitude as that of the ordinary absorption in the crystal; consequently if the crystal is so small that its ordinary absorption for the radiation is negligible (1 or 2 percent), secondary extinction is negligible. The ordinary absorption becomes very small in a crystal as its thickness decreases from 10^{-2} to 10^{-3} cm, and secondary extinction may therefore be neglected in measurements upon crystal powders whose particles are smaller than this lower limit.

Primary Extinction

Primary extinction represents the shielding of lower layers by reflection from the parallel upper layers of the same homogeneous fragment, and takes place only in a perfect crystal. If the perfect crystal block has a thickness greater than about 5×10^{-5} cm, primary extinction is appreciable. Its effect is represented by the fractional correction factor in the expression

$$Q'=Q\frac{\tanh\sqrt{(2Qd^2\cot\theta)/\lambda}}{\sqrt{(2Qd^2\cot\theta)/\lambda}} \tag{2}$$

[2] Darwin, Phil. Mag. **43**, 800 (1922).

Q' is proportional to the measured intensity of reflection and becomes equal to the Q in Eq. (1) when extinction is negligible; d is the thickness of the crystal.

To get some idea of the magnitude of primary extinction, let us evaluate Eq. (2) for rock-salt, using the value of Q' obtained by Bragg, James and Bosanquet[3] for the (200) reflection and corrected for secondary extinction as the Q under the radical. For $d = 5 \times 10^{-5}$ cm, the correction factor is 0.96, while for $d = 5 \times 10^{-3}$ cm, the factor is 0.03. Since the value of Q used to obtain these figures is really a Q' value and may have been reduced by primary extinction, it is evident that these are maximum values of the correction factor. If each powder particle of a sample under investigation is a perfect crystal, the intensity of reflection should vary with the size of the particles until they are less than 5×10^{-5} cm in thickness. Further, the relative intensities from different planes would vary, because the extinction depends upon the intensity of reflection. It will be noticed that primary extinction depends not only upon Q, as does secondary extinction, but also upon $\cot \theta$.

The evidence gathered by Bragg, Darwin and James indicates that most crystals, when subjected to x-ray investigation, are of the imperfect mosaic rather than of the perfect type, and that primary extinction is not very effective; but the fact that a crystal face must be very thoroughly ground before reliable measurements can be made with it, and that grinding invariably increases the intensity of reflection markedly, may be taken to prove that the grinding process has served to convert the reflecting surface of the crystal into a mosaic. Mechanical strains probably break up the crystal blocks near the surface or produce distortions in them which reduce primary extinction. The much more thorough process of grinding a crystal to a powder would therefore be expected to so distort the powder particles that the size of the perfect crystal blocks would be many times smaller than the size of the particles themselves.

There is reason to believe, from evidence which has been gathering from different sources,[4] that even in a crystal which has been subjected to no mechanical strains there is a notable lack of perfection. The mosaic structure is the usual structure for a crystal, with the size of the perfect crystal blocks and their divergence from the mean orientation depending upon the composition of the crystal and upon the mechanical and thermal

[3] W. L. Bragg, James and Bosanquet, Phil. Mag. **42**, 1 (1921).

[4] Mark, Naturwissenschaften **13**, 1042 (1925); Becker, Physik. Zeits **26**, 919 (1925); Smekal, Physik. Zeits. **26**, 707 (1925).

treatment which it has undergone. Estimates of the linear dimensions of the perfect crystal blocks in various substances vary from 10^{-5} to 10^{-4} cm.

Experimental

Measurements of the relative intensities of reflection of the Mo Kα doublet by the different planes of crystal powders of various particle sizes have been made, as well as measurements of the relative intensity of reflection of these different samples with respect to a standard sample of NaCl. The experimental procedure has been described in the preceding paper.

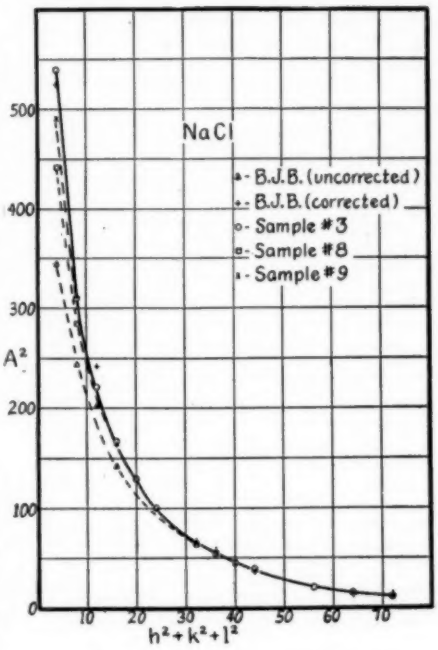

Fig. 1. Comparison of powder method and single crystal measurements on sodium chloride.

Sodium chloride. In order to compare the powder method measurements on NaCl with the data of Bragg, James and Bosanquet on the reflection of Rh Kα radiation by single crystals of rock-salt, it is necessary to make allowance for the difference in wave-length. This is done by expressing the results in terms of the A^2 of Eq. (1), the relative values of A^2 from various crystal planes being independent of wave-length. From expression (2) of the preceding paper, we get, for the powder method

$$A^2 \propto F^2 \propto \frac{P_s}{j} \frac{\sin^2\theta\cos\theta}{1+\cos^2 2\theta} \tag{3}$$

In Fig. 1 the relative values of A^2 are plotted against $(h^2+k^2+l^2)$, the sum of the squares of the Miller indices multiplied by the order of reflection. Extinction, either primary or secondary, should be detected by a change in relative intensities, as is shown by the difference between the corrected and uncorrected curves of Bragg, James and Bosanquet. Variation in the powder method curves must be due to primary extinction, for the particle size was always too small to permit a noticeable effect from secondary extinction.

The data for Fig. 1 are given in Table I. Sample 3 was a powder which had been ground until the particles were all smaller than 4×10^{-3} cm.

The A^2 values are seen to fall upon a smooth curve which coincides with that representing the data of Bragg, James and Bosanquet when the latter are corrected for secondary extinction. Some of sample 3 was ground mechanically for several days (sample 5) until the particle size

TABLE I

Sodium chloride. Values of A^2 in Eq. (1).

Plane	Single crystal (uncorr.)	Single crystal (corr.)	Powdered crystals #3	5	6	7	8	8′	9	9′
111	26	28	26	26						
200	345	524	539	532	546	447	443	505	491	502
220	246	312	310	314	319	296	284	323	315	306
222	203	242	221	214		211			206	
400	142	164	168	170	170	161	163	173	167	166
420			130	134					130	
422			100	100	100	100	100	100	100	100
440	66	68	64							
600, 442		57	56							
620			45							
622		37	39							
444		40								
642			21							
800		14	15.6							
822, 660		12.8	11.9							

was 1×10^{-4} to 2×10^{-3} cm, and gave results identical with those of the original powder. Sample 6, a powder which had passed a 200-mesh sieve and been held back by a 325-mesh sieve, with particle size 4.4 to 7.4×10^{-3} cm, was heated at 760° for 40 hours, then cooled gradually to room temperature. Because of the high vapor pressure at 760° the crystals had grown. After having been reground to their original size, they gave results in agreement with sample 3. Samples 7 and 8 were from the same lot as 6, but were heated at a lower temperature, 700°, for 16 and 46 hours respectively, then cooled slowly to room temperature. The part of the powder which remained between the original limits of size was investigated, care being taken to avoid mechanical strains. The results from these two samples were in close agreement and are plotted in the figure. Evidently sufficient diffusion took place within each powder particle to relieve some of the distortions, and a small amount of primary extinction took place. Analogous results have been obtained by James[5] on heating single crystals of rock-salt. Sample 8, after having been ground for two hours, was reinvestigated (sample 8′) and then gave results in agreement with sample 3. Sample 9 was prepared by condensing the vapor of NaCl which had been vaporized from a hot platinum wire. Most of the particles were about 10^{-5} cm in diameter, being mere points

[5] James, Phil. Mag. **49**, 585 (1925).

when viewed through the oil immersion lens of a microscope, but a few were as large as 3×10^{-4} cm. The measurements show a slight amount of primary extinction, which modified the most intense reflection. Probably crystals formed from the vapor phase are more nearly perfect than those formed from solution, and even though most of the particles were so small that primary extinction in them was negligible, the few larger particles produced an extinction the effect of which was measurable. Although sample 9 was later ground for two hours, there was no change in the intensities of reflection (sample 9′), probably because the particles were so small as to undergo no strains during the grinding.

The results of measurement of the relative intensities of reflection of various samples with respect to the NaCl (220) reflection from NaCl No. 5 are given in Table II. Sample 8 of NaCl here shows no difference from the others, yet in Table I the (200) reflection is found to be reduced 20 percent. A possible explanation seems to be that the measurements of Table II were made three months after the preparation of sample 8 and

TABLE II

Intensity of reflection relative to that from NaCl(200) #5.

The transmission method was used and R_t is $\dfrac{P_{sX}(h\sec\theta\exp[-\mu h\sec\theta])_{NaCl(200)}}{P_{sNaCl}(h\sec\theta\exp[-\mu h\sec\theta])_X}$

Substance	Plane	R_t	Substance	Plane	R_t
NaCl #5,3	200	1.75	CaF_2 #2,3	111	2·18
	220	*1.00*		220	2·44
NaCl #8	200	1.74			
	220	1.01	Calcite #1	211	1·00
NaCl #9′	200	1.65			
	220	1.00			

the measurements of Table I, and after the powder had been several times broken up and compressed; during this period the powder particles underwent sufficient strain to cause them to lose whatever perfection they had gained as a result of the original heat treatment. Sample 9′ shows a definite decrease of reflected intensity in the (200) reflection of about the same magnitude as the decrease indicated in Table I. This sample, it will be remembered, was unaffected by grinding.

Calcium fluoride. James and Randall[6] have measured the relative intensities of reflection of Mo Kα rays from single crystals of fluorite, while MacInnes and Shedlovsky[7] have performed similar experiments with Pd Kα rays. Since the measurements of James and Randall were made with the same wave-length as that used by the author, their results will be utilized for comparison.

[6] James and Randall, Phil. Mag. **1**, 1202 (1926).
[7] MacInnes and Shedlovsky, Phys. Rev. **27**, 130 (1926).

Powder method measurements were made upon three different samples of CaF_2, with results which were in agreement within experimental error. Sample 1 was made by grinding a clear colorless fluorite crystal to 4.4 to 7.4×10^{-3} cm; sample 2 was from the same crystal but was further ground for one day to 4×10^{-3} to 1×10^{-4} cm; sample 3 was a pure precipitated product with particles all smaller than 4×10^{-3} cm. For comparison with the results of James and Randall the powder method values of A^2 are converted into ρ values by the use of the relation, obtained from Eq. (1) and expression (3)

$$\rho \propto \frac{A^2}{j}\sin\theta \qquad (4)$$

The relative values of ρ obtained in this way were plotted against $\sin\theta$ in Fig. 2 so as to agree with the results of James and Randall at large angles of reflection. The data of this figure are contained in Table III. The difference between the two pairs of curves is due to extinction which was operative in the single crystal measurements; whether the extinction was all of the secondary type cannot be definitely decided.

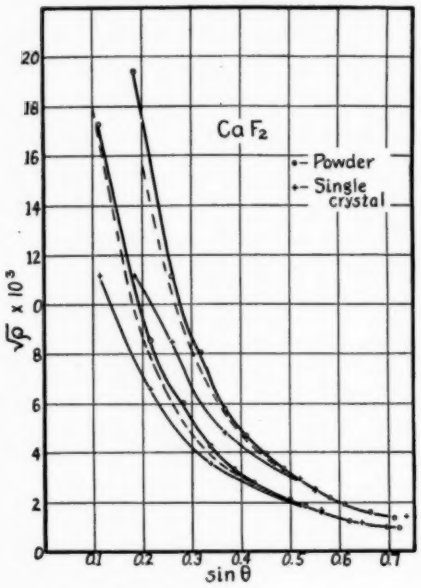

Fig. 2. Comparison of powder method and single crystal measurements on calcium fluoride.

TABLE III

Calcium fluoride

Plane	$\sqrt{\rho}\times10^3$ Single crystal (uncorr.)	Powdered crystals	Plane	$\sqrt{\rho}\times10^3$ Single crystal (uncorr.)	Powdered crystals
111	11·18	17·3	642	——	3·32
220	11·18	19·4	553 / 731	——	2·12
311	6·63	8·55			
400	8·49	11·15	800	2·96	——
331	——	6·03	660	2·47	2·49
422	——	8·06	555	1·67	1·60
333	3·56	4·25	840	——	2·18
440	4·82	5·78	931	——	1·22
531	——	3·33	933	1·18	——
620	——	4·68	862	——	1·60
533	——	2·80	10 42	——	1·35
444	——	3·93	755	——	0·95
			880	1·43	——

James and Randall corrected their results for extinction by assigning to the (111) reflection from CaF_2 an arbitrary F value obtained from the F curve of Ca^{++} given by Hartree,[8] and calculating, on the basis of the difference between the assigned and measured values, a correction factor which was proportional to the measured intensity of reflection. The broken-line curves in Fig. 2 represent their corrected results; the curves are seen to fall definitely below those of the powder method for the more intense reflections. The author's F value for the Ca^{++} reflection at $\sin\theta = 0.1124$ is 15.9, as against Hartree's value of 15.5, and this difference will account for a part of the discrepancy, but the corrected (220) reflection of James and Randall would still be notably weaker than that observed by the powder method.

Calcite. In spite of the difficulty of obtaining accurate powder method measurements because of the proximity of the different reflected beams from calcite, the measurements of Table IV have been made with sufficient accuracy to show clearly the effect of extinction on the single crystal measurements of W. H. Bragg.[9] Sample 1 was a clear calcite crystal which had been ground for several days to particle size of 2×10^{-3} to 5×10^{-5} cm; sample 2, from the same crystal, was ground for only a

TABLE IV

Calcite. Values of A^2 in Eq. (1)

Single crystal		Powdered Crystals						
Plane	A^2 (uncorr.)	Plane	Relative intensity No. 1	No. 2	No. 3	A^2 No. 1	No. 2	No. 3
110	71	110		170			112	
211	395	211	835	841	856	892	898	913
$1\bar{1}0$	153	$1\bar{1}0$	95	94	117	152	151	188
220	147	220				182	209	184
332	263	332	487	562	496	646	745	657
		321				271	312	276
		310				100	100	100
422	100	422	100	100	100	100	100	100
		432				77	77	77
$2\bar{2}0$	89	$2\bar{2}0$	31	30	40	75	73	95
		543				75	73	95

short time, to 7.4 to 4.4×10^{-3} cm; sample 3 was prepared by addition of a saturated solution of ammonium carbonate to a saturated solution of calcium chloride. The crystals of sample 3 were in clusters, 1 to 5×10^{-4} cm in diameter, with the individual crystals much smaller. No attempt has been made to interpret the differences between the powder measurements, these differences being of a much smaller order of magnitude than

[8] Hartree, Phil. Mag. **50**, 289 (1925).

[9] W. H. Bragg, Phil. Trans. Roy. Soc. A. **215**, 253 (1915).

those between the single crystal data and the powder method data. The indices given in Table IV are based upon a unit rhombohedron containing two molecules of $CaCO_3$ with $a_0 = 6.362$ A and $\alpha = 46° 6'$. In the cases where reflections were superposed in the powder method, the total intensity was divided among the components in the ratios suggested by their structure factors as approximated by the ordinary formula used in crystal analysis. The F value for the (211) reflection from sample 1, determined from the data of Table II, is 19.8, while the limiting value for F at $\sin\theta = 0$ for this class of planes is 34. Perhaps the large decrease in F should be taken to indicate that some ordinary extinction is still effective in the powder method results. A. H. Compton[10] determined F for the (211) reflection of a large calcite crystal, his value without any correction for extinction being about 11.

Conclusions

The formula for the intensity of x-ray reflection from an ideally imperfect crystal may be applied without modification to measurements by the powder method, provided that the crystals have been ground to less than 10^{-3} cm in thickness. This conclusion may not hold strictly for a few substances like calcite, which form very perfect crystals. Upon the basis of atomic scattering curves obtained from powder method data, reliable determinations of electron distribution may be made. Further, the correction for secondary extinction as determined and applied by Bragg, James and Bosanquet was satisfactory in the case of rock-salt, while primary extinction was not operative in their experiments. Although experimental determinations of secondary extinction have been made for no other crystals and a rigid test cannot therefore be applied, the indications are that the formula for the ideally imperfect crystal may be applied to most single crystal measurements after the latter have been corrected for secondary extinction.

Jefferson Physical Laboratory,
Harvard University,
July 19, 1926.

[10] A. H. Compton, Phys. Rev. 10, 95 (1917).

DIRECT MEASUREMENT OF X-RAY MASS SCATTERING COEFFICIENT

By Pierre Mertz

Abstract

The mass scattering coefficients for Li, B, C, H_2O and Na at wave-lengths λ .32, .43, .54, .66, .79A were measured directly by collecting the scattered radiation in an ionization chamber surrounding the scatterer, and comparing its intensity with that of a portion of the primary beam going through an auxiliary ionization chamber of equal length along the ray path. The primary beam consisted of the continuous radiation from a Coolidge tungsten tube, filtered through Al and Cu until the spectral width between the half-maximum intensity points was about 25 percent of the mean wave-length. Corrections were made for internal absorption in the scatterer and for the increased absorption of the scattered beam in the ionization chamber due to the Compton effect. The uncertainty in these corrections forms the chief limitation on the accuracy of the measurement. The values of mass scattering coefficient determined are tabulated. The scattering coefficient in all cases starts, for short wave-lengths, below the value computed from Thomson's formula, and slowly increases for longer wave-lengths. For all substances but boron it finally crosses the Thomson value because of gradual entering in of excess scattering.

DIRECT measurements of the mass scattering coefficient of x-rays by measuring the radiation itself were first made by Barkla, and have been repeated with increasing refinement, the more recent determinations being those of Hewlett[1] and Statz.[2] Indirect estimates[3] from the extrapolated intercept (for zero wave-length) of the total mass absorption plotted against the cube (or some power nearly the cube) of the wave-length, have in general given lower values than the direct measurements. Jauncey[4] has recently pointed out that as there are several processes involved in scattering, giving an unmodified beam, a modified beam, and recoil electrons, the scattering coefficient may be separated into three distinct parts. The direct determinations consider only the radiations, while the indirect determinations consider all three parts. The latter should therefore be larger, rather than smaller, than the former.

The present measurements were undertaken to determine the mass scattering coefficient (for the total radiation only) directly by measuring

[1] Hewlett, Phys. Rev. **20**, 688 (1922).

[2] Statz, Zeits. f. Physik **11**, 304 (1922).

[3] Richtmyer, Phys. Rev. **18**, 13 (1921); Hewlett, Phys. Rev. **17**, 284 (1921); Allen, Phys. Rev. **27**, 271 (1926). Some discussion of this is also given in most articles reporting measurements on the total absorption coefficient.

[4] Jauncey, Proc. Nat. Acad. Sci. **11**, 517 (1925).

simultaneously the radiation scattered at all azimuths, thus obtaining more intensity than by usual previous methods (which also determined the azimuthal distribution), and also reducing the number of readings required. A report of these measurements was presented before the meeting of the American Physical Society last April.[5]

Apparatus and Measurements

The ideal form of ionization chamber for the purpose would be a sphere completely surrounding the scatterer and measuring all the radiation scattered (as in Fig. 1a). On account of the mechanical requirements, however, it is convenient to use only a sector of this sphere, taken symmetrically in such a way that the composition of the radiation measured is a true sample of the radiation that would be measured in the entire sphere. The chamber was mechanically built as shown schemati-

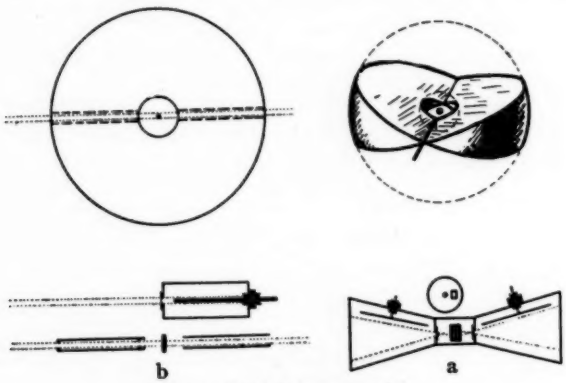

Fig. 1. Ionization chamber.

cally in Fig. 1b, which also shows the comparison chamber above, for comparing the intensity of the scattered beam with that of the primary beam. The length of each chamber along the ray path was 20 cm. Both chambers were used with air at atmospheric pressure.

The electrical connections used are shown in Fig. 2. The electrometer was a Dolezalek type of fairly high sensitivity. The natural leak, which was appreciable because of the large size of the main chamber, was compensated by the small chamber shown here in heavy black, containing uranium oxide and connected in opposition to the main chamber.

The primary beam used consisted of the continuous radiation from a Coolidge tungsten tube, filtered through Al and Cu until the spectral width between the half-maximum intensity points was about 25 percent of the mean wave-length. The estimated spectral distribution of intensity together with the peak voltage and filter, for each of the five beams used,

[5] Mertz, Phys. Rev. **27**, 795A (1926).

is shown in Fig. 3. The point under each curve shows the effective wavelength as measured from the absorbability of the beam in aluminum, from the data given by Richtmyer.[3] The tube was arranged so that the electron stream was at about 45° to the plane of symmetry of the main ionization chamber, to eliminate corrections which would otherwise be required because of the partial polarization of the primary beam.

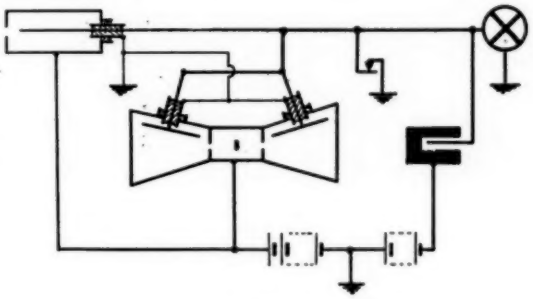

Fig. 2. Electrical connections.

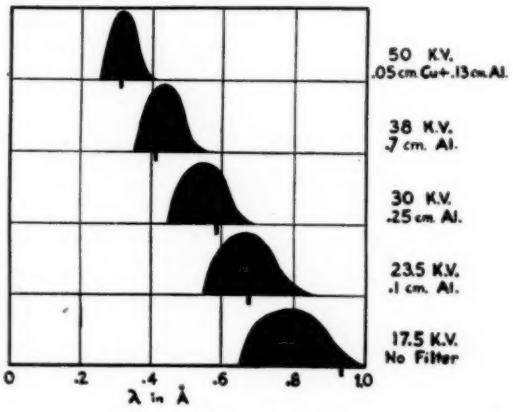

Fig. 3. Spectral distribution of intensity in the primary beam.

The scatterers were in the same form as that used by Hewlett,[1] i.e., a cylinder with axis perpendicular to the primary beam and to the plane of symmetry of the main chamber. The lithium and boron were obtained from Eimer & Amend. The carbon was cut from an arc light carbon containing a total of about 0.05 percent of impurity. The sodium was obtained from the department of chemistry of this university. Those substances which required it were held in capsules similar to those used by Hewlett, but made of thin (.002 cm) paraffined paper. The various samples and capsules varied somewhat in size, but were all about 1/3 cm in diameter, with a length of about 1 cm exposed to the beam.

The readings were taken by measuring the rate of drift of the electrometer needle under the following conditions:

(a) Scattering beam stopped (by suitable piece of lead)
   1. Comparison primary beam stopped
   2. Comparison primary beam measured

(b) Comparison primary beam stopped
   3. Scatterer out of scattering beam (or empty capsule in scattering beam, if a capsule was used to hold the scatterer)
   4. Scatterer in scattering beam

The differences between the rates of drift for cases 1 and 2, and for cases 3 and 4, were proportional to the radiation collected by the auxiliary and main ionization chambers, respectively.

Computations

The scattering coefficient was computed from the following considerations:

The total scattered radiation (J_s) collected by the main chamber when a mass m of scattering substance is irradiated by a primary beam of intensity I, is

$$J_s = Im\frac{\sigma}{\rho}\frac{\phi}{\pi}F$$

where φ is the dihedral angle (in radians) between the planes bounding the sector composing the main chamber, and F is a correcting factor, the ratio between the actual scattered energy getting out of the scatterer and the amount which would get out if there were no internal absorption in the sample.

The radiation (J_p) collected by the auxiliary chamber is $J_p = IA$, where A is the cross-sectional area of the beam entering this chamber. Hence

$$\frac{\sigma}{\rho} = \frac{J_s}{J_p}\frac{A}{m\phi F}$$

The correcting factor F was estimated according to the method used by Hewlett.* It was computed as

$$F = \tfrac{1}{2}(F' + F'')$$

where

$$F' = 1 - \frac{8}{3\pi}b + \frac{3}{8}b^2 - \frac{16}{45\pi}b^3 \cdots;$$

* Hewlett, loc. cit.,[1] §VI, Appendix, pp. 706–08 (1922). Several typographical errors in the appendix to his paper may be noted. The algebraic signs of $y \cos\theta$ and of $y \sin\theta$ should both be $-$ instead of $+$ in both his second and fourth equations. The *numerical* coefficient of the a^3 term in his third equation should be $22/45\pi$ instead of $24/45\pi$.

$$F''=1-\frac{4}{3\pi}\frac{b^2-a^2}{b-a}+\frac{1}{8}\frac{b^3-a^3}{b-a}-\frac{4}{45\pi}\frac{b^4-a^4}{b-a}\cdots;$$

$$a=\tau D;\quad b=\mu D=(\tau+\sigma)D;\quad D=\text{diameter of specimen.}$$

The correction varied from less than 2 percent for Li at $\lambda=.32$A, to 31 percent for Na at $\lambda=.54$A.

A small correction (1.5 percent at most) was made for the absorption of air between the scatterer and the window of the main ionization chamber, as the scattered ray traverses this path in addition to the path traversed by the primary beam.

Since, because of the Compton effect, the scattered radiation is softer than the primary, the ionization chamber will absorb the first more readily than the second, and the main chamber will be more efficient than the auxiliary chamber. It is a complicated matter to compute this correction exactly, as the change in wave-length, intensity ratio between modified and unmodified beams, and total intensity all vary with scattering angle. No data are at present available on the last two quantities for most of the substances and wave-lengths here used. A first approximation to the correction was obtained by assuming all of the scattered beam at all angles to be shifted in wave-length by .0242A. The resulting correction varied from -6.7 to -11.8 percent. The error involved in making the approximations above was estimated in the case of carbon at $\lambda=.712$A, for which Hewlett[1] has studied the azimuthal intensity distribution of the scattered beam, and for which Woo[6] has studied the ratio between the intensities of the modified and unmodified beams. The accurately computed correction is -5.8 percent, as compared with a rough computation of -7.3 percent. In view of the nature of the approximations made, this is probably as close agreement as may be expected. On all of the measurements except those taken at $\lambda=.79$A, and on water and sodium, the accurate correction would be expected to be proportionately larger than in the above example, as the proportion of modified to unmodified scattered radiation increases with decreasing wave-length and with decreasing atomic number. It is therefore probable that for most of the data the discrepancy between the actual and the roughly estimated corrections is not much larger than in the example just considered.

The comparatively large value and uncertainty of the corrections for internal absorption and for the Compton effect form the chief limitations on the accuracy of this method for the measurement of the mass scattering coefficient. The correction for internal absorption limits the use of scatterers to elements not much heavier than sodium. For elements of

[6] Woo, Phys. Rev. 27, 119 (1926).

higher atomic number the size of the sample must be so small, if the correction is to be kept reasonably small, that the scattered radiation is too weak to measure.

Results

The values of mass scattering coefficient as determined are given in Table I:

Table I

Mass scattering coefficient (σ/ρ, in $cm^2/gram$)

Scatterer $\lambda =$	.32	.43	.54	.66	.79A
Li	.133	.165	.157	.169	.200
B	.154	.162	.169	.165	.179
C	.166	.182	.194	.214	.234
H_2O	.198	.206	.210	.216	.228
Na	.173	.191	.248		

These have been plotted in Fig. 4, together with the data obtained by Hewlett[1] and Statz.[2] There is also included in the plot the value of the

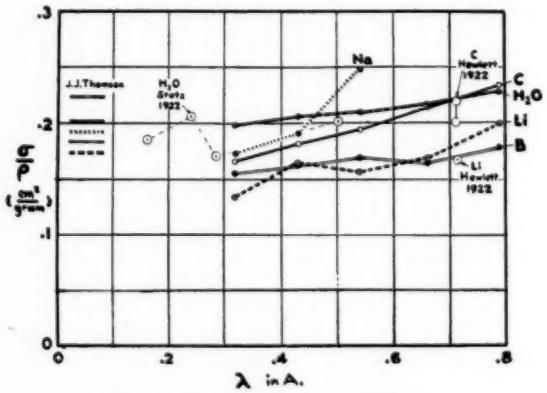

Fig. 4. Mass scattering coefficient.

scattering coefficient for each substance as computed from Thomson's formula.[7] The scattering coefficient in all cases starts, for short wave-lengths, below the Thomson value, and slowly increases for longer wave-lengths. For all substances but boron it finally crosses the Thomson value because of the gradual entering in of excess scattering. The diminished scattering at short wave-lengths explains why indirect determinations of the scattering coefficient from the extrapolated intercept for zero wave-length of the total absorption curve gives consistently low

[7] J. J. Thomson, Conduction of Electricity Through Gases, p. 325 (1906).

results. For the extrapolated value will be less than the value corresponding to any actual point in the data.

It will be noted that if "true" absorption rigorously proportional to the cube of the wave-length is added to a small amount of scattering of which the increase with wave-length is slower than as the cube, the total absorption plotted against λ^3 will give a curve which is not far from a straight line, but is somewhat concave to the λ^3 axis. This slight concavity has uniformly been observed on all measurements of total mass absorption coefficient. From the present discussion it is probably due to a variation of the mass scattering coefficient with wave-length which is of a lower power than the cube (it is almost linear for the present data). This would seem more likely than that the "true" absorption should vary with a power of the wave-length less than the cube. This is all, of course, entirely aside from the more marked variation which is usually observed near the γ ray region.

The author is very glad to acknowledge the inspiration and help given by Professor F. K. Richtmyer in the course of this work.

CORNELL UNIVERSITY,
July 26, 1926.

SOME EFFECTS OF TEMPERATURE ON X-RAY ABSORPTION

By H. S. Read[1]

Abstract

Effect of temperature on the average atomic absorption coefficients of Ag and Ni for x-rays.—The previous results of the author showing a change with temperature of the average atomic absorption coefficients of various metals for x-rays have been confirmed in the case of Ag and Ni. The complete radiation from an x-ray tube operated at 50,000 volts was used. Heating silver to 830°C decreased its transmission about 1.3 percent. Heating Ni to from 700° to 1000°C decreased its transmission about 1.7 percent.

Effect of temperature on the monochromatic atomic absorption coefficient of Ag between λ.275 and .870A.—Spectroscopic resolution of the x-rays passed by a silver absorber alternately heated to 830°C and cooled to room temperature demonstrated a marked variation with wave-length of the effect of temperature on the atomic absorption coefficient. The variation was most marked near the K absorption limit of Ag. On the short wave-length side heating the silver to 830°C increased the atomic transmission about 1 percent whereas on the long wave-length side it was decreased about 1.5 percent. If this change be interpreted as due to an increase in the wave-length of the K-limit, calculation shows the increase to be about 0.21XU.

WHILE testing for evidence to substantiate the statements found in the literature that x-ray absorption is independent of the temperature of the absorber, a surprising result was found.[2] Absorption increased slightly with the temperature. In the former work the total x-radiation from a Coolidge tungsten tube was used but the study has now been continued by measuring the temperature effect for the different wave-lengths and in particular on the short wave-length side of the K-limit of Ni, on both sides of the K-limit of Ag, and on the long wave-length side of the K-limit for Pt. Temperature affected the x-ray absorption quite differently at the different wave-lengths.

Apparatus and Method

The effect of temperature was large enough to measure easily but the effect of thermal expansion also was large and the real change in absorption was a small difference between the measured change, K_m, and the calculated change, K_c, due to expansion only. Since the change in absorption was of the order of one percent consistent results were difficult to obtain. For all experiments one or two assistants accurately adjusted the high voltage and the current supplied to the tungsten Coolidge x-ray

[1] National Research Council Fellow, Stanford University.

[2] H. S. Read, Phys. Rev. **27**, 373 (1926).

tube.[3] It was possible to hold the high voltage constant to one part in 3000 and the current constant to one part in 20,000, and to measure the x-rays in the ionization chamber to one part in 3000. However, for unknown reasons, the measured x-ray intensities frequently varied by over 1/10 percent.

The apparatus may be described as follows. A Coolidge, tungsten-target, x-ray tube was placed in a lead box in such a manner that the focal spot was a vertical line source of x-rays through a vertical slit in the box. The relay that timed all exposures moved a lead block in front of or away from this first slit. Next came the thin absorber. It was 10 cm long, 2.5 cm wide, and from 1 to 2×10^{-3} cm thick. Two small V-shaped crooks bent into the absorber allowed it to heat up and expand nicely without any detected warping. The absorber was placed horizontally, on edge, and was clamped near the ends into two heavy brass uprights. The clamps were provided with jaws of nickel to prevent corrosion. The uprights were parts of a rigid frame that was moved up and down on guides so that the absorber was either just below the x-ray beam or squarely across and more than covering the beam. The absorber was heated to incandescence by a large 60 cycle alternating current from a step-down transformer and cooled to room temperature by an electric fan. The higher temperatures were measured with a Siemans and Halske optical pyrometer and these temperatures did not vary measurably over an area twenty times larger than the x-ray beam. Two .001 cm Al screens, 8 cm square, were placed on the two sides of and 1 cm from the absorber to keep heat away from the lead slits, spectrometer, and crystal.

The unabsorbed part of the x-ray beam passed on to a second slit only 1.0 mm wide, thence to a calcite crystal on a spectrometer table, on to a third slit, 4.0 mm wide and equally distant from the crystal, and into a large ionization chamber to be absorbed there in methyl-bromide, in the usual manner.

A second ionization chamber with equal and opposite voltage on it was used to neutralize the effects of a very small ionization current due to some natural penetrating radiation. No x-rays entered it.

During an exposure of the order of 30 seconds timed to 1/300 second the unabsorbed x-rays were reflected from the calcite crystal and ionized the gas in one chamber. As the chamber rod and string electrometer wire charged up, the electrometer showed a deflection. The deflection was counteracted by changing the voltage on the second ionization chamber just sufficiently to bind all the collected charge onto the rod there. The

[3] The high voltage circuit used was a development of that first described by D. L. Webster, Proc. Nat. Acad. Sc. **6**, 28, 269 (1920).

x-ray intensity was recorded in terms of voltage change necessary to keep the electrometer deflection at zero. This method had the advantage that the voltage on the working ionization chamber never changed and any slight lack of saturation voltage there caused no effect. The counteracting voltage was measured accurately by use of a calibrated galvanometer with a 4000 mm scale at 5 meters distance. The usual galvanometer deflection was from 2000 to 3000 mm which was equivalent to an electrometer deflection of 200 to 300 divisions. Thus although the electrometer never moved appreciably it was reset to zero to within one part in 2000 to 3000, i.e., to a tenth of one division. The electrometer had a sensitivity of 200 divisions per volt on the string but only 50 divisions per volt on the second ionization chamber.

The measurements of x-ray intensity with the absorber below the beam and across the beam gave data used to calculate the absorption coefficient in the usual way. While the absorber was held in place across the beam alternate measurements of x-ray intensity for the absorber cool and hot indicated the percent increase of transmission due to heating, K_m.

The expected percent change, K_c, due to the thermal expansion of part of the absorber out of the beam, was calculated. In the well known transmission equation

$$I = I_0 \epsilon^{-\sigma n x}$$

we need only remember that an, which includes a density factor, changes inversely as the cube of the dimension and that x changes directly as the first power of the dimension. The linear dimension of the absorber changes with temperature in a manner represented by the equation

$$L_t = L_0(1+\alpha T+\beta T^2) = L_0(1+g)$$

Let W_1 be the total transmitted intensity for a cool absorber and W_2 for it when heated. The percent increase in transmission due to heating may be defined as $(W_2-W_1)/W_1$. Using the approximations

$$(1+g)^{-2} = 1-2g, \qquad e^{2ganx} = 1+2\ ganx$$

we get approximately, assuming the change in transmission to be due solely to thermal expansion,

$$K_c = 2\ ganx$$

The *measured* percent change of transmission, K_m, does not seem to equal K_c and this unaccounted for difference (K_m-K_c) is here reported as due to an intrinsic change with temperature of the atomic absorption coefficient of the absorber. The values of K_m-K_c are shown in tables and curves.

Precautions

Several precautions were needed to insure and to test the accuracy of the method, and to expose experimental errors. Heat from the absorber was kept away from all other parts by the two thin Al screens. Successive runs with the absorber heated were made without the alternate cooling to learn whether the leakage of heat to the absorber holders expanded them enough to move the absorber as a whole or not, but no effect was found. A test was made to learn if the magnetic effect of the absorber heating currents and the heat lost from the absorber to the air, Al screens, and to the supports had any effect. For this test the absorber was lowered to a position just below the x-ray beam and while there alternate readings were taken with the absorber cool and hot. The averages of the two sets of readings were equal to within one part in 3000. This indicates that the above mentioned causes produced only negligible effects.

An attempt was made to learn whether or not the change of absorption which included scattering was due to a change in scattering. The absorber was placed across the x-ray beam as usual and the unabsorbed x-rays reflected. After a plot was made of the distribution of the x-ray beam at the ionization chamber with the crystal fixed, the chamber was set just off the beam where it received scattered and perhaps a small amount of reflected x-rays. These scattered x-rays had 0.04 of the intensity of the main x-ray beam. Alternate readings with the absorber hot and cold were nearly equal. If there is any change of scattering with temperature it was not one-tenth large enough to explain the change of absorption. However, this test does not prove that there is no temperature effect on scattering.

Second order reflections were not present except in a few cases not reported here and then the change of transmission due to heating was some average value for the two wave-lengths.

Results

1. *Change of absorption.* The results are best shown in the form of tables and curves. Table I shows the coefficients of expansion that were used, copied from Landolt and Bornstein, 5th edition, p. 1228. It is quite possible that the metals used here, because of their state of purity or because of rolling, had slightly different coefficients of expansion. The metals were purchased from Eimer and Amend. Any error in calculated expansion would change the result but could not account for the variation in the change of absorption with wave-length.

TABLE I

Coefficients of expansion used.

$L_t = L_o(1+\alpha T+\beta T^2)$

	α	β	Range
Nickel[4]	13.460×10^{-6}	35.15×10^{-10}	500–1000°C
Silver	18.270	47.93	0– 875°C
Platinum	8.868	13.24	0–1000°C

Two attempts were made to compare the results of the new system of measurement with those of the former paper.[2] With the ionization chamber directed straight into the slit system at the x-ray tube target and with the calcite crystal removed, all the wave-lengths of the x-ray spectrum were used. Since in the previous work 50 kilovolts a.c. was used on the tube and in the present work 50 kilovolts d.c. the energy spectra are different but as nearly alike as was possible. The new values agree with the old values more nearly than was expected, Table II and Fig. 1.

TABLE II

Check on previous results.

All wave-lengths from the x-ray tube at 50,000 volts d.c. were used.

	T	$2g$	anx	K_m	K_e	K_m-K_e	Note
Ag	20–830	.0359	.989	.0225	.0355	−.0130	new
	20–830	taken from published curve				−.0180	old
Ni	20–764	.0236	1.41	.0182	.0333	−.0151	new
	20–880	.0280	1.42	.0233	.0396	−.0163	new
	20–1000	.0328	1.42	.0262	.0465	−.0203	new
	20–764	taken from published curve				−.0140	old
	20–880	redrawn after omitting the				−.0165	old
	20–1000	880° point.				−.0190	old

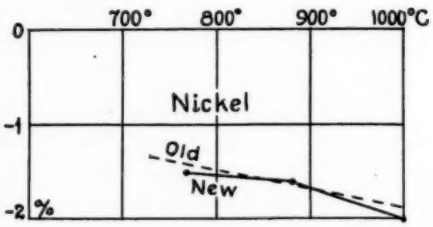

Fig. 1. Decrease due to heating of the total transmission of x-rays by nickel. Dotted curve shows previous work; solid line curve shows present work.

The final measurements are represented in Table III and in the solid line curve in Fig. 2. For some wave-lengths measurements were repeated and the average value is plotted. The dotted curve represents preliminary tests during the development work on the apparatus. It is less reliable and yet shows clearly the same general shape. Experiments at shorter

[4] Also Scientific Papers of the Bureau of Standards **17**, 500 (1922), gives these values for nickel.

TABLE III

Change of transmission of silver when heated from 20° to 830°C

λ	*anx*	K_m	K_e	$K_m - K_e$
.275A	.540	.0194	.0194	.0000
.330	.860	.0265	.0309	−.0044
.330	.748	.0270	.0246	−.0024
.366	1.07	.0300	.0386	−.0086
.385	1.18	.0538	.0427	.0109
.385	1.18	.0435	.0423	.0012
.403	1.31	.0500	.0472	.0028
.437	1.63	.0689	.0586	.0103
.437	1.68	.0627	.0605	.0022
.457	1.84	.0718	.0664	.0054
.457	1.87	.0735	.0669	.0066
.457	1.82	.0725	.0657	.0068
.457	1.72	.0631	.0620	.0011
.475	1.95	.0725	.0703	.0022
.475	1.87	.0665	.0673	−.0008
.493	.627	.0136	.0225	−.0089
.500	.649	.0192	.0234	−.0042
.510	.447	.0142	.0164	−.0022
.510	.458	.0090	.0165	−.0075
.545	.509	.0223	.0183	.0040
.650	.792	.0236	.0285	−.0049
.755	1.12	.0338	.0402	−.0064
.870	1.35	.0259	.0450	−.0141

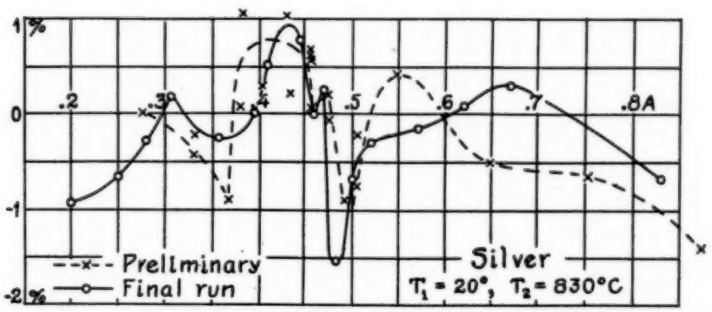

Fig. 2. Variation with wave-length of the increase in transmission of a silver absorber heated to 830°C.

wave-lengths failed because the higher required voltage was very difficult to maintain constant on account of corona loss and leakage. At times the services of two experienced assistants adjusting voltage and current were not sufficient. Experiments at longer wave-lengths failed because the x-ray intensity was too small to measure accurately. Greater resolution could easily have been attained by simply reducing the slit widths. However, the 1.00 mm slit used was a practical minimum since that much x-ray intensity was required to allow intensity measurements to better than 1/10 percent.

2. *Change in the K-limit.* The observed change in transmission through Ag for wave-lengths very near the K-limit was very marked. If it is due to a change in the K-limit the change can be calculated. F. K. Richtmyer[5] has shown that the K-limit is an abrupt break as shown in Fig. 3. Consider the case in which the slit admits wave-lengths and intensities bounding the areas A_1 and A_2. The energy transmitted is $A_1+A_2=A_C$ or A_H, when cool or hot. Since I_1 is approximately $1/6\ I_2$

$$A_C=\tfrac{1}{2}SI_1+\tfrac{1}{2}SI_2=3.5\ SI_1$$

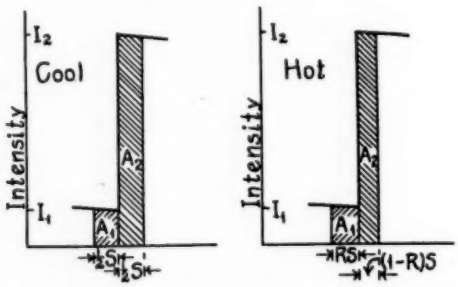

Fig. 3. The K-limit shift is used to account for the observed decrease in transmission near the K-limit of Ag.

When hot the division is not half the half but R and $(1-R)$ say.

$$A_H=RSI_1+(1-R)SI_2=(6-5R)SI_1$$

The measurements show $A_C=1.015\ A_H$. Thus $R=.510$ and $R-.500=.010$. Heat shifted the limit $.010S$ toward longer wave-lengths.

The actual curve was not like Fig. 3 but had the usual rounded corners. The difference in crystal angles for the maximum and minimum points was used to calculate the range of wave-lengths covered by the slit. Here the slit covered 0° 15′ or 21XU. Thus the shift was .010×21XU =0.21XU, a very small amount. Since the limit, 485XU, requires 25,400 volts the shift corresponds to 11 volts. The heat of molecular agitation at 830° C corresponds to less than one volt.

The above hypothesis suggests that heat aided the quanta in ionizing atoms in some undescribed way, that a smaller quantum was able to ionize a hot atom. If this hypothesis is established a slight shift in the emission spectrum and the short wave-length limit toward shorter wave-lengths should occur when the target of the tube is allowed to heat up to incandescence as is common. Scattered x-rays from a hot scatterer might likewise be of slightly shorter wave-length than the primary x-rays or than the x-rays from a cool scatterer. The writer does not know of any

[5] F. K. Richtmyer, Phys. Rev. **26**, 724 (1925).

other measurements to substantiate the hypothesis but points out that only very accurate measurements would show such a small shift of wave-length.

It appears that a very critical test might be made by comparing the measured transmissions through a hot and cool Ag absorber of a K line from an Ag target tube. If the shift suggested above is real the absorber on being heated up should transmit more of any K line, even more of an increase than thermal expansion would suggest.

D. L. Webster has suggested a photographic method. If a plate is exposed to reflected general or white radiation the plate will be darkened about 6.0 times more on the shorter wave-length side of the K-limit than on the long wave-length side, due to absorption in the emulsion. If a silver absorber of the right thickness is interposed it will neutralize the effect and give a uniformly exposed plate. Now if heating the absorber shifts its K-limit to a longer wave-length a narrow line of less exposure should appear on the plate. The heated absorber should be surrounded by some inert gas or a vacuum and the wall of the chamber carefully kept at constant temperature.

3. *Change in absorption.* In the previous paper[2] it was shown that if a' and a are the average atomic absorption coefficients at the temperature T and at room temperature respectively, the results are fairly well represented by the equation

$$a' = (1+g)a,$$

where

$$1+g = 1+\alpha T+\beta T^2$$

This was based on measurements at several temperatures and on several metals for which $2K_m = K_c$, approximately. The present relation is not so simple. Here

$$K_m = M_\lambda K_c$$

and M_λ is greater than unity for some wave-lengths and less than unity for others. Using as a good approximation of K_c the expression 2 *ganx* it can be shown that $a' = (1+g)a$ should be replaced by the more general

$$a' = [1-g(2-M_\lambda)]a$$

This gives at best an inadequate idea of the change of absorption and in fact no explanation of the phenomena is offered.

It does not seem possible to explain the change in terms of a shift of the white spectrum because for each wave-length the voltage was adjusted so that the wave-length used came near the flat topped maximum of white x-radiation.

The writer wishes to express his best thanks for help and guidance received from Professors F. K. Richtmyer, A. H. Compton, P. A. Ross, and D. L. Webster, and to the National Research Council for the fellowship which made this work possible.

STANFORD UNIVERSITY,
September, 1925.

THE ABSORPTION OF X-RAYS FROM λ=.08 TO 4.0A

By S. J. M. Allen

Abstract

The mass-absorption coefficients of a number of elements from C to U for homogeneous rays from λ.709 to 1.933A and for filtered general rays from 1.93 to 4.0A have been measured. A Shearer gas tube, continuously pumped and arranged with a controlled side leak was used. The data from these observations, together with those from the two previous papers by the author at wave-lengths from λ.08 to .709A taken with the same apparatus and on the same samples throughout, form a set of continuous results from .08 to 4A, from which, after a careful analysis, the following conclusions can be stated. Over a wide range of wave-lengths, in which the mass-scattering coefficients σ/ρ can be neglected, the *fluorescent absorptin coefficients* τ/ρ cannot always be represented by the generally accepted formula, $o\tau/\rho = C\lambda^n$ with n and C constant, but each element must be considered by itself, with values of n and C changing rather abruptly in certain regions of wave-length. In general the values of n which best fit the results are a high value 2.92 and a low value 2.6. Nowhere does λ^3 over a long range accurately represent the data. Over the complete range of wave-length, the *absorption of* Al appears to be quite accurately represented by the formula, $\mu/\rho = (13.9 \text{ or } 14.0)\lambda^{2.92} + (.14 \text{ to } .18)$ and is therefore well suited as a standard substance for the determination of effective wave-lengths from absorption coefficients. *The N^4/A law*, although holding fairly well in those cases where n is the same for all the elements involved, can at best be only approximate, and it therefore does not seem possible to express the absorption of x-rays by a universal formula of the form $\tau/\rho = C\lambda^3 N^4/A$, in which C is a constant. *The discontinuity magnitudes*, $J_K = C_K/C_L$, extended to Fe, show steadily increasing values with decrease of atomic number N, reaching a maximum value for Fe of about 10. For the L-M series, $J_L(=C_L/C_M)$ shows values following the same law as J_K does, with probably somewhat higher values for the same elements than J_K. For the M-N series, $J_M(=C_M/C_N=10$ to 12 in the case of U) apparently indicates that J_M with five discontinuities has much higher values than J_L or J_K for the same elements. The effect of impurities in the cases of Al, Cu, Sn and Pb was ascertained, and only the presence of Fe in the Al could make an error as great as 1 percent.

Introduction

IN TWO recent papers,[1,2] the author gave the results of measurements on the mass-absorption coefficients μ/ρ of a number of elements from carbon to uranium, over a range of homogeneous wave-lengths from λ.08 to λ.709A. The chief conclusions of these papers may be briefly summarized as follows.

(a) As λ decreases, the fluorescent absorption coefficient τ/ρ, becomes less and less important, while the scattering coefficient σ/ρ becomes more

[1] Allen, Phys. Rev. **24**, 1 (1924).
[2] Allen, Phys. Rev. **27**, 3 (1926).

and more important, and also in the case of the light elements, when τ/ρ has practically disappeared, σ/ρ decreases very slowly, if at all, with further decrease of λ.

(b) A careful analysis of the data, by trial and error, or by means of graphs, indicates that τ/ρ can be expressed approximately as a function of λ, in the form, $\tau/\rho = C\lambda^n$, if the proper values of σ/ρ are first subtracted from the experimental values of μ/ρ. The author was of the opinion that the value of n which best represented the results was smaller than the generally assumed value 3, being on the average about 2.92. The assumed values of σ/ρ increased with the atomic number and also slowly with λ, reaching in the case of the high atomic weight atoms, values as great as 1.0. The N^4/A law held well for all the elements, except those of high atomic weight.

(c) The magnitudes of the K discontinuities were shown to be smallest for the heavy atoms, and increased with decrease of N, the range being from about 5 for Pb to from 7 to 8 for Ag.

The conclusion (c) has also been confirmed in general by the important work of Richtmyer, who in a recent paper,[3] with a spectrometer of high resolving power investigated the K discontinuities of Pb, Au, W, Sn, Ag, and Mo. His values from Pb to W are somewhat larger than those of mine, as stated in the first paper, but are in better agreement with mine of the second paper, which appeared just after that of Richtmyer. The revised values of mine, which will be discussed later in the present paper, are in even better agreement with those of Richtmyer. In any case there is good agreement as to the general phenomena involved. In obtaining his values of the discontinuity magnitudes Richtmyer draws his graphs, assuming the truth of the λ^3 law. However over the short range necessary it would not make any great difference if $\lambda^{2.92}$ had been used. He states from his data that the following formulas will hold good for Sn and Ag.

$$\mu/\rho_{Sn} = 90\lambda^3 + 1.0; \quad \mu/\rho_{Ag} = 70\lambda^3 + 1.0$$

These formulas indicate rather high values of σ/ρ for Sn and Ag, those of the author from the $\lambda^{2.92}$ relation being about half as great. Again Richtmyer gives values of σ/ρ for Pb, Au and W about .85, less than those of Sn and Ag, which would be a somewhat peculiar result.

Any of these formulas, if correct, should predict at λ1.0A the actual experimental value of μ/ρ, since we would have $\mu/\rho = C + \sigma/\rho$ or $\tau/\rho = C$. I shall discuss this question more fully later on.

A number of theoretical formulas of absorption have been deduced on various assumptions, and they all involve as a necessary part, the λ^3 law.

[3] Richtmyer, Phys. Rev. **27**, 1 (1926).

Richtmyer, at considerable length, very clearly analyzes the formulas of Thomson, de Broglie, and Kramers, as to their agreement with experimental facts. The agreement is certainly not very good for any one of them.

Certain European writers of books on x-rays evidently consider that the λ^3 does not always represent the facts. Siegbahn, in his well known book on the spectroscopy of x-rays, gives a table of absorption coefficients, which do not indicate λ^3. Ewald in his book on Roentgen Ray Spectra states that the law of absorption follows more correctly $\lambda^{2.80}$.

Since practically all the data, by various observers using homogeneous rays, upon which the λ^3 law is based, lie in the range from $\lambda.1$ to .7A, where in most cases, the unknown values of σ/ρ are an important part of the whole, it would seem difficult to decide the question satisfactorily in this region.

In view of this, and the importance of the question, the author has carried out during the past winter measurements on the mass-absorption coefficient μ/ρ of elements from *C* to *U*, for homogeneous rays from $\lambda.709$ to $\lambda 1.933$A, and for specially filtered rays, from $\lambda 1.93$ to λ4A. With these long wave-lengths σ/ρ becomes negligible (except for *C*, and in some cases Al), and μ/ρ becomes approximately equal to τ/ρ.

Experimental Arrangement

These experiments were carried out with the same spectrometer, equipped with two Soller collimators, that was used in the previous experiments on shorter wave-lengths. Also the absorbing layers were made from the same materials. They therefore form a set of data from .08 to 4A with the same apparatus, on the same samples, and by the same experimenter, and whatever may be the probable errors of the combination, they should at least be somewhat free from the uncertainties introduced when one attempts to compare the data obtained by different observers, with different samples of substances of unstated purity. The variation of τ/ρ with λ, as ascertained from the data, should be more consistent.

Two chief difficulties were encountered, a slight variation of the tube during observations, and the lack of homogeneity of the excessively thin layers necessary for the long wave-lengths. Many readings and weighted means reduced the former to a minimum, and careful rolling with a good hand roll finally obtained quite satisfactory layers of the elements. With the collimator method a larger area of the layer exposed to the rays can be used, in contrast to the single narrow slit method. In general the area of the layer was just a little greater than the area of the window through

which the rays were coming. The average mass per unit area through which the rays penetrated was thus nearly the same as that obtained for the whole layer by weighting. In the few cases where the layers were much larger in area than the window, they were removed around in different positions to obtain an average.

For all cases from λ.709 to λ1.933A several layers of every element were used and complete absorption curves obtained. The average value of μ/ρ from the complete curve was chosen. In the case of Sn from 1.93 to 4A, only one layer was thin enough to be used. The mass per unit area of this layer was obtained by weighing, and also by calibrating it against other thicker layers of the same material, in regions of shorter wave-lengths.

The uranium layer was made in the following manner. Metallic uranium was ground to fine powder, suspended in alcohol with a trace of shellac, flooded into a layer of filter paper, and allowed to dry. A portion of this layer which seemed by examination to be the most homogeneous was so marked that it could in each measurement be placed in the same position in front of the window. Every reading for the absorption at each wave-length was thus taken through the same area. A layer of the same filter paper was also measured at the same wave-length, and from the percentage absorptions of the two layers, the net absorption of the uranium could be readily calculated.

The mass per unit area of the uranium was not found by weighing, but an effective value was obtained, by assuming that the N^4/A law held between uranium and Pb in the M absorption for the same chosen wave-length. Knowing μ/ρ for Pb, the percentage absorption of the uranium layer, and the assumed ratio between uranium and Pb, the mass per unit area of the uranium layer was calculated. Even though the absolute values of μ/ρ for uranium obtained in this manner may be in some error, such an error would be a constant one, and not affect the relative values.

A number of the substances were chemically analyzed for me by Dr. Gray of the Bureau of City tests, of this University, and the effect of impurities will be discussed presently.

The source of radiation for these experiments was a Shearer gas tube, manufactured by Adam Hilger Co., London. This tube is of metal with a glass cylindrical tube separating cathode from anode. Targets of various metals can be easily interchanged. All parts which would become heated are water cooled. The tube during operation is kept continuously pumped, with a side air leak, controlled by a fine capillary tube, rubber tube and pinch cock. For a given current strength, once equilibrium has been obtained between pump and leak, no further attention for hours is

necessary except occasionally a touch of the pinch cock. A milliammeter in the tube circuit indicates constancy of current. The source of potential was a small transformer, the tube itself acting as a good rectifier. By means of impedance coils in the primary, any secondary voltage between 3000 and 40,000 was readily obtainable.

The Kα and Kβ radiations of Fe, Ni, Cu, and Zn were used, together with the general radiations for wave-lengths between .709 and 1.293A. The intensities of the characteristic rays were of course much greater than the general radiations, but in all cases the intensities were great enough to be measured to an accuracy of 1 percent. Care was exercised, to be sure that no higher orders were present. The (100) planes of a calcite crystal was used as the reflecting crystal. A large number of readings with different settings of the spectrometer at λ1.0A were made.

For observations between λ1.93 and 4A, an attempt was made to isolate narrow portions of the general spectrum by crystal reflection, but not enough intensity could be obtained for measurement. I have as yet no targets beyond Fe. So, in order to obtain approximate information on the absorption of wave-lengths beyond the Kα of Fe, filtered rays had to be used, the effective wave-lengths estimated from the absorption in Al, which the homogeneous observations had shown to be a constant relation between τ/ρ and λ.

Two methods of "filtering" were employed, the ordinary "end rays" method, and a method which may be called "filtering from both ends." The first was used in those cases where, in the general radiation, no components were present whose wave-lengths were the same as any of the discontinuity wave-lengths of the substance used as an absorber. Aluminum was used as the filter in those cases.

The second method was used to obtain approximately homogeneous radiation on the long wave-length side of any of the discontinuities. For example, in examining the M absorption of Sn close to the L_1, discontinuity, a filter of Al was used to cut down the long wave-lengths, and a filter of Sn to cut down the short wave-lengths beyond L_1, the small remainder being quite homogeneous. By then varying the tube voltage a range of effective wave-lengths could be obtained. For Ag-M absorption, a filter of Al+Ag was used, and for U-N absorption, a U filter. In all cases a companion measurement in Al was made of such a nature that the total absorption in Al was the same as that for the element in question. In short, the absorption in any substance is being compared with the same total absorption in Al.

It is easy to show, both theoretically and by numerous experimental examples, that under these prescribed conditions, the relative absorption

coefficient of any substance to that of the standard substance, is the same as would be obtained if homogeneous rays had been used. To illustrate this point, the results expressed in Table I are given. In the first set the values of μ/ρ for the homogeneous radiation λ1.93A is compared for a number of substances with an Al+Fe filtered beam of the same effective λ. In the second set, the filter is Al+Cu. Within experimental errors the comparative values are the same. In the second set it is to be noticed that Ni is passing through its K discontinuity for this filtered beam.

TABLE I

Comparison between μ/ρ for homogenous, and filtered rays

Radiation	C	Al	Fe	Ni	Cu	Zn	Ag	Sn	Pt	Pb
Homogeneous $\lambda=1.93$	9.2	94	71	90	99	115	410	490	365	420
Filtered $\lambda=1.93$	9.3	94–95	72	92	100	116	415	485	360	425
Homogeneous $\lambda=1.45$	4.5	41.5	294	335	43.5	52	197	241	176	207
Filtered $\lambda=1.45$	4.4	42	295	$K\gamma$	44	51	200	240	178	205

For wave-lengths up to λ2A, the thin aluminum window furnished with the tube was sufficiently thin to transmit the rays, but for longer wave-lengths recourse had to be had to a less absorbing substance. Considerable difficulty was experienced, but finally thin windows of celluloid and gelatine were found satisfactory.

EXPERIMENTAL RESULTS AND DISCUSSION

The mass-absorption coefficients μ/ρ with homogeneous rays for the substances, paraffine wax, carbon, iron, nickel, copper, zinc, silver, tin, tungsten, platinum, gold, and lead, are expressed in Table II. The range of wave-lengths is from the Kα of Mo to the Kα of Fe. The results with

TABLE II

Values of μ/ρ for homogeneous rays reflected from calcite (100)

	K			L						M			
λ	Par-affine	C	Al	Fe	Ni	Cu	Zn	Ag	Sn	W	Pt	Au	Pb
1.933A	8.0	9.2	94	71	90	99	115	410	490		365		420
1.752	5.9	7.3	73.2	56	69	76	90	325	385		280		335
1.655	5.1	6.4	61.5	430	60	64	76	280	275		243	265	290
1.537	4.1	4.9	48.5	330	47.5	50	59	225	325		199	210	230
1.432	3.5	4.3	40.3	290	323	42.0	50.5	192	235	130	171	179	202
1.389	3.1	3.8	36.0			38.0	45.0	173	205		155		180
1.293	2.6	3.2	29.8	213	237	266	38.0	146	176	105	131	137	154
1.170	2.1	2.4	22.5	160	175	206	226	113	132		100	104	120
1.090	1.7	2.0	18.5	128	148	165	186	95	110		87–88		98
1.000	1.25	1.50	14.2	102	118	133	152	73	87		165	110	177
.910		1.25	10.8	75	88	102	115	57	66		170	165	150
.748	.73	.76	6.20	45.0	55	61	69	33.0	39.0		134	141	145
.709	.60	.63	5.29	38.4	47.0	52.0	59	26.8	32.5		117	122	140

filtered rays are shown in Table III, the range of wave-lengths being 1.08 to 3.93A. In discussing the results with homogeneous rays it will be advantageous to place them in certain groups.

TABLE III

Values of μ/ρ for strongly filtered "end rays" from general radiation. λ calculated from Al, $\tau/\rho = 14\lambda^{2.92}$

λ effective	K absorption			L absorption				M		N
	Paraffine	C	Al	Fe	Ni	Cu	Zn	Ag	Sn	U
3.93A			760					540	680	490
3.74			660	510		666		570	610	424
3.66			620	490		624			560	410
3.44			516	394		530		660	460	564
3.37			485	374	460	496	590	700	440	580
3.22			426	338	402	430	534	1000	390	600
3.18			410	322	388	420	500	1100	420	600
3.04			360	284	340	364	430	1100	600	600
2.97			338	270	320	350	420	1150	660	600
2.60	17.0	21.5	225	176	210	230	276	870	980	570
2.49			200	156	190	206	246	806	910	560
2.35			170	132	160	176	210	720	780	540
2.24	11.5	14.7	148	113	142	156	182	640	715	525
2.18			136	105	128	144	172	585	660	516
2.06			116	90	110	120	144	510	560	495
1.97			101	79		112		490	505	485
1.93			94	72	92	100	116	415	485	470
1.80			80							442
1.54			48						250	360
1.45		4.4	42	29.5	Kγ	44	51	200	240	285
1.24			26.5						150	190
1.08			18.0							150

Group (1). Those light substances whose absorption lies wholly in the K series. In this group, aluminum is the most useful element to discuss. The chemical analysis of the aluminum used shows Al 99.4 percent, Fe 0.4 percent, Si 0.15 percent. The only impurity present which will have any appreciable effect upon μ/ρ for Al is the Fe, and its effect for all values of λ less than the Kγ of Fe has been calculated as about 1 percent, about equal to or a little greater than the experimental error. For values of λ greater than Kγ the effect would be much less than the experimental error. The effect of the silicon would also be negligible.

In analyzing the data for Al, the mass-scattering coefficient σ/ρ has been taken from the previous papers as .14 to perhaps .18. Except for the shorter wave-lengths its effect will not greatly affect the discussion.

The analysis of Al by the "trial and error" method is shown in Table IV where one vertical column gives the values of C in the formula, $\tau/\rho = C\lambda^n$, for $n = 3$, and the other column, those for $n = 2.92$.

Very few data are available to establish the value of μ/ρ for Al at 1.0A, but what there are show values generally between 14 and 15. Hewlett's[4]

[4] Hewlett, Phys. Rev. **17**, 284 (1921).

results would indicate at λ1.0A a value about 14 or a little less. The weighted average of the author's results at λ1.0A lies between 14.1 and 14.2, which, subtracting the value of μ/ρ, would give a value of $\tau/\rho = 13.95 - 14.00$. The effect of the iron impurity would be to make this value for pure Al 1/2 to 1 percent smaller, considering our average experimental error as less than 1 percent. It is very probable therefore that the value of C for pure Al is close to 14.0, perhaps slightly less. Any formula then should predict at λ1.0A a value of C close to 14.0.

Contrasting in Table IV the values of C for $n=3$ and $n=2.92$, we see that $n=3$ gives at short wave-lengths, values of C close to 15, and at

TABLE IV

Values of C in equation, $\tau/\rho = C^{\lambda}$ for various values of n which best fit the data.

λ	Al				Cu			Sn		Pb		
	$n=3$	$n=2.92$	$n=3$	$n=2.92$	$n=2.7$	$n=3$	$n=2.92$	$n=2.6$	$n=3$	$n=2.92$	$n=2.6$
.430	15.0	14.0	155	144	120	94	87	68	482	450	343
.500						92	87				
.525						92	87				
.560	14.3	13.7	150	143		90	85				
.600						90	87				
.631	14.4	14.0	149	143	130	91	88		400	380	
.650						90	87				
.675						91	88				
.710	14.4	14.0	145	141	131	88	86	78	400	380	350
.750	14.4	14.1	145	142	130	89	87				
.850	14.4	14.1	138	137		86	85				
.910	14.0	13.9	134	133	131	87	86				
1.000	14.0	14.0	132	132	132	87	87	87	77	77	77
1.109	14.2	14.3	128	129	131	85	86	90	76	76	78
1.170	13.9	14.1	129	130	134	83	84	90	75	76	80
1.293	13.6	14.0	119	123	130	81	83	90	71	72	78
1.389	13.3	13.7	14.1	14.5	15.6	76	80	89	67	68	77
1.432	13.6	14.0	14.4	14.6	15.8	79	82	92	69	70	79
1.537	13.3	13.8	13.7	14.2	15.7	76	78	90	63	66	75
1.655	13.7	14.1	14.3	14.6	16.4	73	75	88	64	67	78
1.752	13.5	14.2	14.0	14.7	16.7	71	74	90	62	65	77
1.933	13.1	13.7	13.7	14.4	16.8	68	72	89	58	61	76

long wave-lengths values close to 13, a steady systematic decrease; while $n=2.92$ gives values, which though fluctuating + and −, are on the average close to 14.0. It is very evident, to the author at least, that the λ^3 law does not express the results over this range of long wave-lengths. Whether $\lambda^{2.92}$ expresses them completely over this range, or whether there may be a slight change in the function of τ/ρ with λ, would take precision work with absolutely pure Al to decide. Certainly aluminum comes the nearest to showing a constant function of τ/ρ with λ of any of the substances studied. It therefore is well chosen as a standard for estimating effective wave-lengths, over a very wide range.

A considerable amount of work has been done by other observers at the Kα of Mo, λ.709 to .710A. Most of these give values of C from 5.27 to 5.30. Taking 5.28 as an average, and solving for C we obtain, for $n=3$, a value 14.4, and for $n=2.92$, a value 14.0.

At the characteristic radiations of Fe, λ1.752 and λ1.933A, we get for $n=3$, a value for C of 13.3, and for $n=2.92$, a value for C of 14.0, a difference between the two of about 7 to 8 percent.

The graphs for Al, for $n=3$, and $n=2.92$ are shown in Fig. 1.

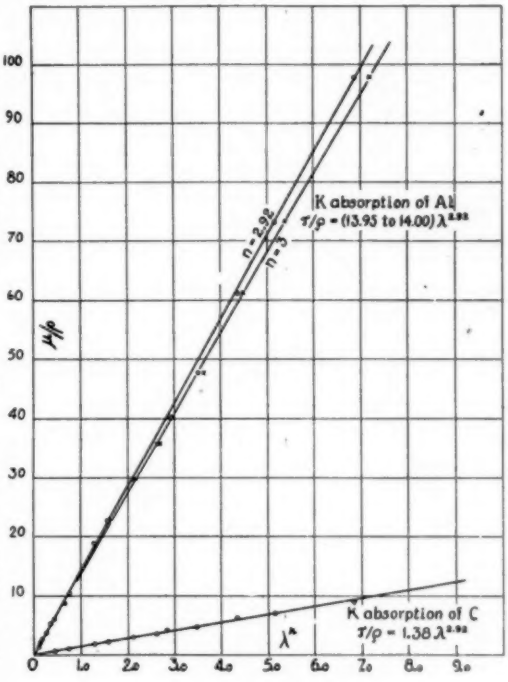

Fig. 1. μ/ρ against λ^n.

Carbon and paraffine wax are apparently following the same law as aluminum, the C of carbon being on the average a little more than 1/10 the value for Al. Paraffine wax, which the author in the previous paper on very short wave-lengths showed had a value of μ/ρ greater than that of carbon, in this present range of wave-lengths has values less than those of carbon. The effect of the richness of hydrogen in paraffine upon the scattering coefficient has been discussed there.

Group (2). Elements, whose absorptions lie partly in the K and partly in the L series. This group comprises Fe, Ni, Cu and Zn. Of these, Cu was chemically analyzed as Cu 99.83 percent (no Sn, Zn, or Pb present). This is very pure Cu, and any traces of impurities can not effect results. The analyses of these four elements shows in each case the same characteristics, viz., $n=3$ does not fit the data over the complete range, nor does $n=2.92$, but the function of τ/ρ with λ in the K absorption seems to be made up of two distinct functions, a higher value of n for short wave-lengths, and lower values for long wave-lengths near Kγ.

The results for Cu are chosen for illustration, and are shown in Table IV. It is seen that $n=3$ gives values of C steadily decreasing, both in the

K and L absorptions. $N=2.92$ fits the results well up to a certain value of λ, after which a smaller value of n seems best.

The data of the past, notably that of Richtmyer,[5] and Stoner and Martin,[6] on the λ^3 law would predict a value of C at $\lambda 1.0$ in the neighborhood of 150 for Cu. The actual experimental value by the author at 1.0A is about 132 or 133, a much smaller value. Data of the past on Zn would predict for C at 1.0A values from 160 to 170, while the experimental value is about 152. This apparent rather sharp break in the function in these four elements occurs at a value of λ less than 1.0A which accounts for the predicted values always being greater than the experimental.

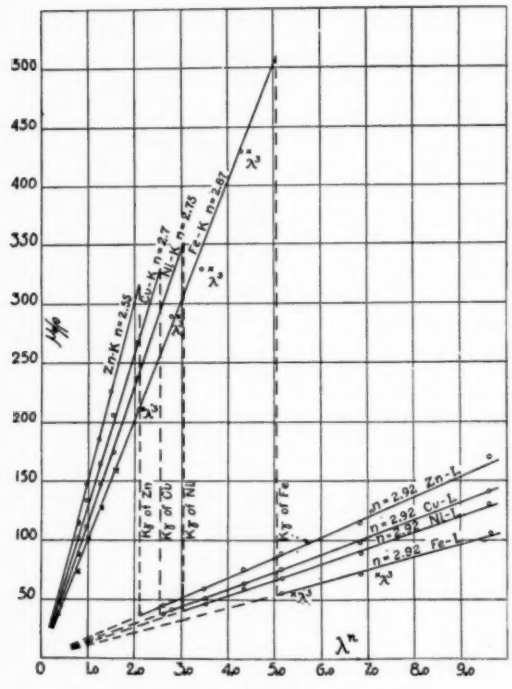

Fig. 2. μ/ρ against λ^n.

Very few data are at hand by other observers above 1.0A for these elements, but what there are show on analysis to be of the same general character. All I can find in the literature are a few scattered results of Bragg and Pierce,[7] a few results of Hewlett on Fe, and the original classic results of Barkla. It is noteworthy that in Hewlett's graph of Fe, is shown this "break" and he calls attention to it.

The author's data for the L absorption of these elements, shows that $n=2.92$ holds extremely well, and also that if these graphs are produced backward they pass very close, if not actually through, the origin. In fact $\lambda^{2.92}$ seems in all cases to be the only graph that will do this. Barkla's data if translated into effective wave-lengths equal to the mean of $K\alpha$ and $K\beta$ are in very good agreement with those of the author. In Fig. 2 will be found the graphs, showing the relation of τ/ρ to λ, for the four elements.

[5] Richtmyer, Phys. Rev. **18**, 13 (1921).
[6] Stoner and Martin, Proc. Roy. Soc. **A 107**, 312 (1925).
[7] Bragg and Pierce, Phil. Mag. **8**, 608 (1914).

Group (3). Those elements whose absorptions lie wholly in the L series. These include Pd, Ag, and Sn. The results for Pd are not shown, because they indicated below λ1.1A a sudden increase to values somewhat above those of Ag, which is undoubtedly caused by the presence of platinum as an impurity. Above λ1.1 the data for Pd are of value since the M absorption of Pt is nearly the same as the L absorption of Pd. The Ag consisted of both commercial and very pure samples, and no difference was detected in the values of μ/ρ over the entire range. The chemical analysis of Sn, gave Sn 99.81 percent (no Sb, Cu or Pb), which indicates high purity. The analysis of the results on Sn is shown in Table IV for $n=3$, $n=2.92$, and $n=2.6$. From λ.43 to λ.71A the data used for calculation include all the data from the papers of Richtmyer, Stoner and Martin, and Bragg and Pierce, the average value being chosen. It is seen again that $n=3$ does not hold, but $n=2.92$ holds very well up to about λ1.2A, when a value of $n=2.6$ fits most satisfactorily. We have again this "break," but it now occurs above 1.0A, which results in the predicted value of C from short wave-length data being less than the actual value at λ1.0, just the reverse of what occurs for Cu. We can now test Richtmyer's formulas for Ag and Sn, quoted in the introduction to this paper. In the case of Sn the formula would predict at λ1.0A a value of C about 89 or 90, which is in fair agreement with the actual value, but at λ1.933 it would predict a value of 649, which is about 32 percent greater than the experimental value. The formula for Ag would predict values with just as great a discrepancy. The graphs for Ag and Sn are shown in Fig. 3, and Fig. 4, for $n=3$, 2.92, and 2.6.

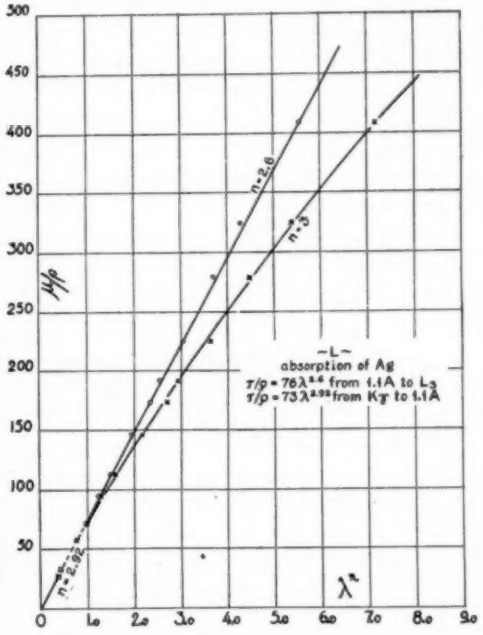

Fig. 3. μ/ρ against λ^n.

Group (4). Those elements whose absorptions lie wholly in the M series. This includes W, Pt, An, and Pb. The analysis of the results for Pb is shown in Table IV. The chemical composition of the lead samples was Pb 99.83 percent (no Sb or Sn) which is very pure. It is seen that neither $n=3$ nor $n=2.92$ fit the results, except possibly near λ1.1A, but

that $n=2.6$ fits very well. If the 2.6 graph is produced backward it will pass above the origin indicating that probably a "break" to the 2.92 graph occurs about 1.1A. Any evidence of this "break" at shorter wave-lengths is hidden by the L discontinuities. However, all these elements in their L absorption (which includes the M) show better agreement with $n=2.92$ than a lower value of n. (See second paper.) In Fig. 5 and Fig. 6 are shown the graphs for Pt and Pb.

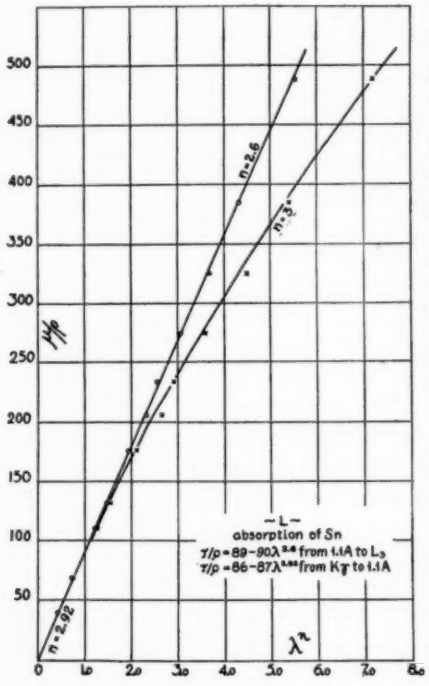

Fig. 4. μ/ρ against λ^n.

The data for the filtered rays from Table III have been analyzed in the same manner as already discussed for the homogeneous radiation. The graphs are shown in Figs. 7 and 8. Aluminum being chosen as the standard substance from which to calculate the effective wave-lengths, cannot be directly analyzed. The only data available to compare it with are two values of Barkla (the $K\alpha+K\beta$ of Cr, and the $K\alpha+K\beta$ of Ca), and the data of Miller,[8] who used filtered general rays and calculated his wave-lengths from the minimum quantum wave-lengths, which would of course be too low. Taking the effective wave-lengths of Barkla's rays as 2.18A and 3.22A we obtain for $n=3$ values of $C=14.2$ and 14.4, in very good agreement with the author's for homogeneous rays. If Miller's effective wave-lengths are chosen as about 9 or 10 percent greater than the minimum quantum wave-lengths we obtain an average value

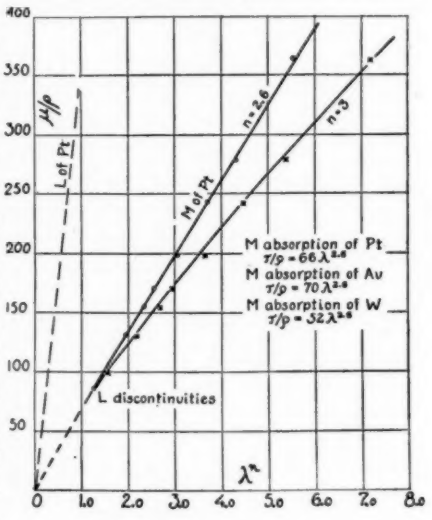

Fig. 5. μ/ρ against λ^n.

[8] Miller, Phys. Rev. 8. 329 (1926).

of C about 13.9. On the whole there is very good evidence that Al is continuing to function as it did for shorter wave-lengths.

The results for Fe, Ni, Cu and Zn form a continuation of the data for homogeneous rays, being absorbed according to the 2.92 law, and having the same values of C. Ag and Sn continue to be absorbed approximately according to $n=2.6$ up to a point where the nearness of the L discontinuities affect the data. In the case of Sn, the M absorption apparently follows once more the 2.92 law, being in this respect similar to what occurred in Cu when it passed through its Kγ. Only one value in the M absorption of Ag was obtained, so its variation in the M absorption cannot be stated, but is assumed to be the same as that in the case of Sn. The data for uranium would indicate that it is being absorbed in the M series according to the $\lambda^{2.6}$ law, and in the N absorption according to the 2.92 law (data rather meager). It is interesting to note that at a wave-length of 4A, uranium is mass for mass more transparent than aluminum (U being in the N, and Al in the K series).

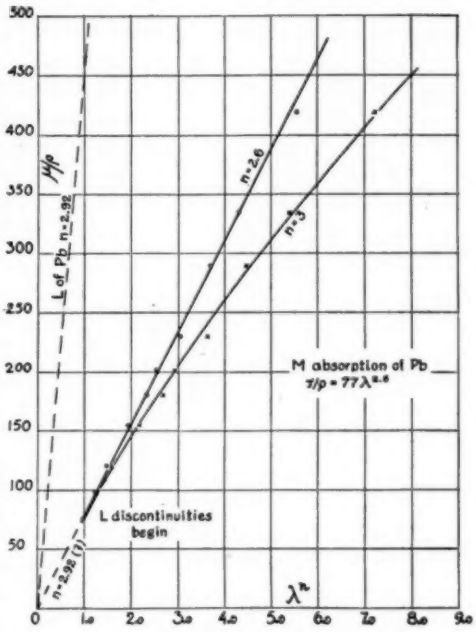

Fig. 6. μ/ρ against λ^n.

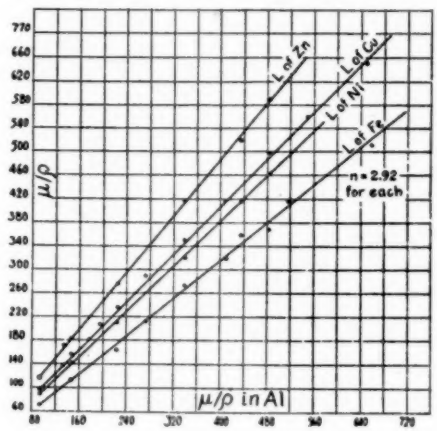

Fig. 7. μ/ρ against μ/ρ_{Al} for filtered rays.

The complete data of this paper and the two previous ones are summarized in Table V, which gives a complete experimental history of the absorption of x-rays from $\lambda.08$ to $\lambda4.0$A. The range is the approximate region within which the chosen values of N and

C hold good. The values of the discontinuity magnitudes "J" are calculated from the values of $C(J_K = C_K/C_L,\ J_L = C_L/C_M,\ J_M = C_M/C_N)$. Since there are several values of C corresponding to the different series, I have given the greatest and the least.

TABLE V

Summary of analyses of data.
$\mu/\rho = \tau/\rho + \sigma/\rho$, $\tau/\rho = C\lambda^n$, J is the discontinuity magnitude at the K, L, or M absorption edge, $J = C_K/C_L$ or C_L/C_M or C_M/C_N

Element	Range	Series	C	n	J Max	J Min
C	.08 to 2.6A	K	1.38	2.92	Not known	
Al	.08 to 3.93A	K	13.95 to 14.00	2.92	Not known	
Fe	.08 to .6A	K	104 to 108	2.92	10	9.5
	.6 to Kγ	K	102	2.87		
	Kγ to 3.74A	L	10.7	2.92		
Ni	.08 to .8A	K	128 to 132	2.92	9.8	8.8
	.8A to Kγ	K	116 to 118	2.75		
	Kγ to 3.37A	L	13.3	2.92		
Cu	.08 to .85A	K	142 to 144	2.92	9.8	9.1
	.85A to Kγ	K	132	2.70		
	Kγ to 3.74A	L	14.5	2.92		
Zn	.08 to .9A	K	162 to 165	2.92	9.5	8.8
	.9A to Kγ	K	152	2.6 ?		
	Kγ to 3.24A	L	17.25	2.92		
Ag	.08A to Kγ	K	540 to 580	2.92	7.7	7.3
	Kγ to 1.10A	K	73	2.92		
	1.10 to 2.50A	L	76 to 78	2.6	8.0	7.5
		M	10.0	2.92		
Sn	.08A to Kγ	K	650 to 670	2.92	7.6	6.9
	Kγ to 1.20A	L	86 to 87	2.92		
	1.20 to 2.50A	L	89 to 90	2.6	7.5	7.0
	L_1 to ——	M	12 to 13	2.92		
W	.08A to Kγ	K	1840	2.92	6.4 or less	
	Kγ to L	L	285	2.92		
	L to about 1.0A	M	52	2.92	5.5	5.5
	about 1A to M	M	52	2.6		
Pt	.08A to Kγ	K	2000 to 2300	2.92	6.0	
	Kγ to L	L	345	2.92		
	L to about 1.1A	M	65	2.92	5.3	5.2
	about 1.1A to M	M	66	2.6		
Au	.08A to Kγ	K	2000 to 2300	2.92	5.8	
	Kγ to L_3	L	360	2.92		
	L_1 to about 1.1A	M	69	2.92	5.2	5.1
	about 1.1A to M	M	70	2.6		
Pb	.08A to Kγ	K	2000 to 2400	2.92	5.0	
	Kγ to L_3	L	440	2.92		
	L_1 to 1.15A	M	77	2.92	5.7	5.6
	1.15A to M	M	76 to 78	2.6		
U						
	1.0A to M_5	M	110 to 120	2.6	10 to 12	
	M_1 to ——	N	9 to 10	2.92		

It has already been shown that in the K-L series, J_K is least for atoms of high atomic weight and increases as N decreases. Formerly J_K was only known to Mo, but we have now the values for Zn, Cu, Ni and Fe, which as seen show a still further increase to a maximum value near 10. For the L-M series we have values of J_L for Pb, Au, Pt, W, Sn and Ag, which indicate the same kind of phenomena as has been observed for J_K. The values of J_L seem on the whole to be somewhat greater than the corresponding values of J_K. The one value for J_M, that of U, would indicate that U in passing from the N absorption to the M through its five discontinuities "jumps" 10 or 12 times.

If J_M behaves like J_K and J_L the N-M "jumps" for the lighter elements must be very large. J_K for U is about 4–5, and J_L about 5. It must be considered, however, that this estimated J_M for U is derived from data which may not be free from objection, and that homogeneous rays, and a homogeneous metallic layer of U might give different results. It is merely given here as an interesting possibility from the only data at hand at present.

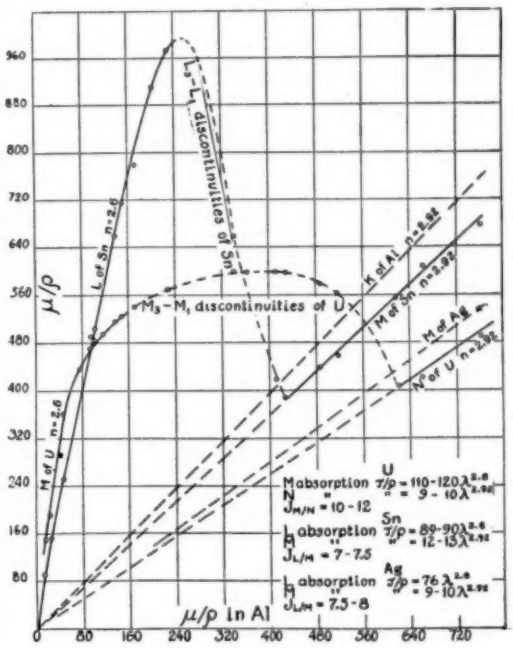

Fig. 8. μ/ρ against μ/ρ_{Al} for filtered rays.

Conclusion

The author is convinced from a study of the data of this paper and that of the two previous ones, that the process of absorption of x-rays over a wide range of λ and N is not simple, and not capable of being always represented accurately by a simple formula of the type $\tau/\rho = C\lambda^n$ in which n and C remain constant, but that each element is a law by itself, changing at certain regions rather abruptly its functionality. This change may occur in the K, L, M, etc., series depending on the atomic number of the substance.

Since both J and n change with the elements, the N^4/A law can at best be only approximate.

The theoretical formulas of absorption, whose derivation necessitates the λ^3 law, would seem to have great difficulty in fitting the present experimental facts. It is too early yet to attempt to give theoretical explanations of the phenomena herein described, but the empirical relations given in the summary may be very useful in predicting the absorption coefficients of any elements not included in the tables.

It can be shown in several cases that the absorption of a low series of an element of high atomic weight is the same as that of the next higher series of some element of lower atomic weight, which again is the same as that of a still higher series of a still lower element. For example, the N absorption of U, the M absorption of Ag or Pd, the L absorption of Mn, and the K absorption of Na or Mg are about the same, and all probably obey the $\lambda^{2.92}$ relation, while the M absorption of U, the L absorption of I, and the K absorption of Ni, are about the same, and follow the $\lambda^{2.6}$ relation.

The author is at present engaged in perfecting means of obtaining more homogeneous rays beyond 2A, and is also awaiting the arrival from Kahlbaum of samples of chemically pure elements in thin sheets, so that the present results can be checked at a few properly chosen wave-lengths by methods of greater precision.

UNIVERSITY OF CINCINNATI,
June, 1926.

STRIPPED YTTRIUM (Y_{III}) AND ZIRCONIUM (Zr_{IV})

By I. S. Bowen and R. A. Millikan

Abstract

Hot spark spectra of yttrium and zirconium.—Using aluminum electrodes, first with yttrium oxalate and borax fused into their cores, and second with zirconium hydroxide replacing the yttrium oxalate, the hot spark spectra of Y_{III} and Zr_{IV} have been identified and the series relationships and term values analyzed. The results are tabulated. In these stripped atoms the normal position of the electron is in a $4d$ orbit rather than in a $5s$.

IN PRECEDING work we have presented the spectral relationships of the stripped atoms of the elements contained in the first two rows of the periodic table, and in this laboratory with the aid of our apparatus, J. A. Carroll[1] has extended this sort of analysis to some of the elements in each of the three rows beginning with copper, silver, and gold, respectively.

In the present paper we extend the same process to the row beginning with rubidium, taking the appropriate data from the literature for

TABLE I

Series lines of Y_{III}

Int.	λ(I. A. Vac.)	ν	Δν		Term values		
1	989.21	101090.8	726.5	$4d_2-4f$	$5s$	157822.9	
2	996.37	100364.3		$4d_1-4f$	$6s$	78572.6	
1	2128.66	46977.9	1553.1	$5p_2-5d_2$	$5p_1$	122335.0	
2	2191.84	45623.8	199.0	$5p_1-5d_1$	$5p_2$	123888.7	
1	2201.44	45424.8		$5p_1-5d_2$	$4d_1$	164565.8	
1	2206.73	45315.9	1553.2	$5p_2-6s$	$4d_2$	165289.2	
1	2285.05	43762.7		$5p_1-6s$	$5d_1$	76711.4	
5*	2328.06	42954.2	723.4	$4d_2-5p_1$	$5d_2$	76910.4	
20*	2367.94	42230.8	1553.7	$4d_1-5p_1$	$4f$	64200.0	
15*	2415.43	41400.5		$4d_2-5p_2$			
30*	2817.86	35487.9	1553.8	$5s-5p_1$			
20*	2946.89	33934.1		$5s-5p_2$			

* The intensities and wave-lengths of these lines were taken from Exner and Haschek.

[1] Carroll, Phil. Trans. Roy. Soc. 225, 357 (1926).

rubidium and strontium and, for the first time presenting, with the aid of our own work, the spectral relationships of the stripped atoms of yttrium and zirconium.

Taking new hot spark spectra, first, when the aluminum electrodes have had a mixture of yttrium oxalate and borax fused into their cores, and, second, when zirconium hydroxide has replaced the yttrium oxalate and using the general method of procedure which we have fully explained in preceding articles we have obtained the results shown in the following Tables I and II, and again summarized in very condensed form in Table III.

TABLE II

Series lines of Zr_{IV}

Int.	λ(I. A. Vac.)	ν	Δν		Term values	
1	628.65	159071.0	1235.2	$4d_2-4f$	$5s$	238545.9
2	633.57	157835.8		$4d_1-4f$	$6s$	124291.1
2	1183.97	84461.6	1253.8	$4d_2-5p_1$		
4	1201.81	83207.8		$4d_1-5p_1$	$5p_1$	192344.4
4	1219.88	81975.3	2486.3	$4d_2-5p_2$	$5p_2$	194827.4
0	1417.66	70538.8	1488.0	$5p_2-6s$	$4d_1'$	275553.3
1	1469.49	68050.8		$5p_1-6s$	$4d_2$	276803.5
2*	2164.43	46201.5	2483.0	$5s-5p_1$	$4f$	117725.0
2*	2287.36	43718.5		$5s-5p_2$		

TABLE III

Comparison of term values

	$N=$	4	5	6
	$R/N^2=$	6858.44	4389.40	3048.19
s	Rb		33689.1	13557.9
	Sr/4		22238.1	10304.0
	Y/9		17535.9	8730.3
	Zr/16		14909.1	7768.2
p_2	Rb		21110.2	9974.1
	Sr/4		16309.3	
	Y/9		13765.4	
	Zr/16		12176.7	
d_2	Rb	14334.3	7988.9	5002.4
	Sr/4	18598.9	8916.6	5357.5
	Y/9	18365.5	8545.6	
	Zr/16	17300.2		
f	Rb	6897.6	4418.2	3068.0
	Sr/4	6990.1	4474.0	3103.0
	Y/9	7133.3		
	Zr/16	7357.8		

The plotting of the atomic number against the $\sqrt{\nu/R}$ values corresponding to the *s*, *p*, *d*, and *f* terms in the case of these four elements yields the Moseley diagram shown in Fig. 1. This is like the other Moseley diagrams which we have presented in the field of optical spectra save in two particulars, namely:

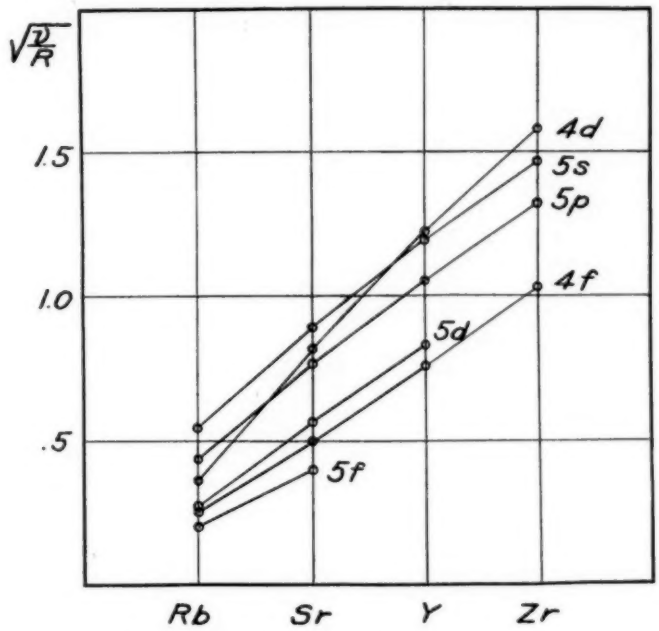

Fig. 1. Moseley's law in the field of optics.

(1) the lines corresponding to the 4*d* and 4*f* terms are seen in Fig. 1 to be no longer parallel, and hence they appear to violate the irregular doublet law,[2] and

(2) the 4*d* line starts at rubidium below the 5*s* and 5*p* lines and rises above these lines in progressing from rubidium to zirconium. This obviously means that while an electron is less tightly bound in rubidium in the 4*d* level than in the 5*s* or 5*p* levels, in yttrium and zirconium these relations are reversed and an electron is most tightly bound in the 4*d* level. *In other words, in yttrium and zirconium the normal position is in a 4d orbit rather than a 5s orbit. This is the first time that a stripped atom has been observed in which the lowest level, and hence the rest position, of the electron has not been an s orbit.*

The lack of parallelism in Fig. 1 between the 4*d* and 4*f* lines, i.e., the failure of the irregular doublet law, is explained as follows. This law

[2] Bowen and Millikan, Phys. Rev. **24**, 209 (1924).

should hold only when the screening constant σ for each of the two orbits involved is the same for atoms of adjacent atomic number. Such a change in the screening constant as must occur when with increasing atomic number the $4d$ level changes from a non-penetrating to a penetrating orbit of course destroys at once the irregular doublet law.

CALIFORNIA INSTITUTE OF TECHNOLOGY,
PASADENA.
July 28, 1926.

THE HYDROGEN SPECTRUM IN THE NEW QUANTUM THEORY

By Carl Eckart*

Abstract

The *Born and Jordan matrices* representing the "coordinates" of the hydrogen atom are calculated. The model is that of an electron revolving without rotation about a positive nucleus. The computation is based on a method developed independently by the author and by E. Schroedinger. *Half quantum numbers* appear in the formulas for the matrices. It is stated without proof, that they also enter into the formula for the *relativistic fine structure*. This will necessitate the consideration of a more elaborate model for the hydrogen atom (the rotating electron of Uhlenbeck and Goudsmit). The *intensity ratio* of the two brighter components of H_α is calculated and found to be 10:2.1 in contradiction with the observed 10:8. For H_β the calculated ratio is 10:3.6, and the observed 10:9. The discrepancy is too great to be accounted for by the incompleteness of the model, and points to a difficulty in the Born and Jordan theory.

E. SCHROEDINGER[1] and the author,[2] independently, have developed a method for calculating the Born and Jordan matrices. The method is based on an equation proposed in two earlier papers by Schroedinger.[3] In this paper it is proposed to apply it to the determination of the matrices which are supposed to represent the hydrogen spectrum.

The simple model of an electron revolving about a positive nucleus will be the basis for the calculation, in so far as any model is involved. The possibility that the electron itself may be in rotation will not be considered,[4] though it is believed that it will be necessary to make this assumption if a satisfactory account of the fine structure is to be obtained.

The fundamental equation of the theory of the hydrogen atom is, according to the work of Schroedinger (Ref. I):

$$\frac{h^2}{8\pi^2 m}\Delta^2\psi+\left(\frac{e^2}{r}-W\right)\psi=0 \qquad (1)$$

where m and e are the mass and charge of the electron and W the energy of the stationary state. Schroedinger has discussed, in a very elegant

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[1] Schroedinger, Ann. der Physik **79**, 734 (1926) (communicated March 18, 1926). This paper will hereafter be referred to as Ref. II.

[2] Eckart, Proc. Nat. Acad. **12**, 473 (1926) (communicated May 31, 1926); Phys. Rev. **28**, 711 (1926). The last paper will be referred to as Ref. A.

[3] Schroedinger, Ann. der Physik **79**, 361, 481 (1925), hereafter cited as Ref. I.

[4] Uhlenbeck and Goudsmit, Nature **117**, 75 (1926).

manner, the solutions of this equation which are to be considered as physically admissable, so that it will be sufficient to quote his results.

These solutions correspond to values of W in (1) which are given by

$$W=-\frac{2\pi^2me^4}{h^2l^2}, \quad l=1,2,3,\cdots. \tag{2}$$

These values are recognized as the Bohr energy levels. The solutions themselves are

$$\Psi=B\chi(nl,r)P_n^m(\cos\theta)\exp(im\phi) \tag{3}$$

where $r\theta\phi$ are the usual polar coordinates. The functions P_n^m are the functions associated to the Legendre polynomials, and m and n are integers, m ranging from $-n$ to $+n$.[5] The quantity B is an arbitrary constant, whose value will be determined later.

The function χ satisfies the equation

$$\frac{d}{dr}\left(r^2\frac{d\chi}{dr}\right)+\left\{\frac{8\pi^2m}{h^2}(Wr^2+e^2r)-n(n+1)\right\}\chi=0 \tag{4}$$

and may be represented by the integral

$$\chi(nl)=\frac{r^n}{2\pi i}\int\exp(zr)\cdot\left(z-\frac{1}{\rho l}\right)^{l+n}\left(z+\frac{1}{\rho l}\right)^{n-l}dz \tag{5}$$

which is to be evaluated along a closed path, in the complex plane, which encircles the point $z=-1/\rho l$. The quantity ρ has the value $h^2/4\pi^2me^2$. By Cauchy's formula, this integral reduces to zero when $n>l$, and to

$$\chi(nl)=\frac{r^n}{(l-n-1)!}\left(\frac{\partial}{\partial z}\right)^{l-n-1}\left\{\exp(zr)\cdot\left(z-\frac{1}{\rho l}\right)^{l+n}\right\} \tag{6}$$

when $n<l$. In (6), the quantity z is to be given the value $-1/\rho l$ after the differentiation has been carried out.

Preliminary Formulas

In the next section, we shall require certain integrals, which will be discussed here, so as not to break the continuity of the later steps. The first integral is

$$\int_0^\infty r^2\chi(nl)\chi(n\lambda)dr \tag{7}$$

It is readily deduced from (4), by partial integration, that it is zero unless $l=\lambda$. In this last case, formula (6), together with the formula

[5] Cf. Byerly, Fourier Series and Spherical Harmonics, p. 195.

$$\int_0^\infty x^n e^{-ax}dx = n!/(a^{n+1}), a>0$$

yields

$$\int_0^\infty r^2[\chi(nl)]^2dr = \frac{(2n+2)!}{[(l-n-1)!]^2}\left(\frac{\partial^2}{\partial z\partial y}\right)^{l-n-1}\frac{\left[\left(z-\frac{1}{\rho l}\right)\left(y-\frac{1}{\rho l}\right)\right]^{l+n}}{(-z-y)^{2n+3}}$$
$$= [c(nl)]^2, \tag{7a}$$

where both z and y are to be replaced by $-1/\rho l$ after the differentiations have been carried out. Substituting $p=l-n-2$, $q=2n+2$, $\zeta=\rho lz$, $\eta=\rho ly$ this becomes

$$\left(\frac{1}{\rho l}\right)^{2n-1}\frac{q!}{[(p+1)!]}\left(\frac{\partial^2}{\partial\zeta\partial\eta}\right)^{p+1}\frac{[(\zeta-1)(\eta-1)]^{p+q}}{(-\zeta-\eta)^{q+1}} \tag{8}$$

Using Leibnitz's formula

$$\left(\frac{\partial}{\partial x}\right)^p AB = \sum_{\alpha=0}^{p}\frac{p!}{\alpha!(p-\alpha)!}\frac{\partial^{p-\alpha}A}{\partial x^{p-\alpha}}\frac{\partial^\alpha B}{\partial x^\alpha} \tag{9}$$

expression (8) reduces to

$$\left(\frac{1}{\rho l}\right)^{2n-1}\frac{(p+q)!}{[(p+1)!]^2}\left(\frac{\partial}{\partial\eta}\right)^{p+1}(\eta-1)^{p+1}\frac{\partial}{\partial\zeta}\frac{(\zeta-1)^q(-\eta-1)^p}{(-\zeta-\eta)^{p+q+1}} \tag{10}$$

The factor involving ζ is

$$\left\{\frac{(\zeta-1)^{q-1}}{(-\zeta-\eta)^{p+q+1}}+(p+q+1)\frac{(\zeta-1)^q}{(-\zeta-\eta)^{p+q+2}}\right\}$$

Substituting $\zeta=-1$ in this, since all the differentiations have been carried out, and the result into (10), we have as the value of the integral

$$-\left(\frac{1}{\rho l}\right)\frac{(p+q)!}{[(p+1)!]^2}\frac{\partial^{p+1}}{\partial\eta^{p+1}}(-\eta+1)^p =$$
$$(2)^{q-1}\left\{q\frac{1}{(1-\eta)}-2(p+q+1)\frac{1}{(1-\eta^2)}\right\} \tag{11}$$

To reduce this further, we evaluate

$$\left(\frac{\partial}{\partial\eta}\right)^{p+1}\frac{(\eta+1)^p}{(1-\eta)^\alpha}$$

for $\eta=-1$. By Cauchy's formula, this is

$$\frac{(p+1)!}{2\pi i}\int\frac{(\eta+1)^p d\eta}{(\eta+1)^{p+2}(1-\eta)^\alpha} = (p+1)!\frac{\partial}{\partial\eta}(1-\eta)^{-\alpha} \tag{12}$$

Evaluating this for $\eta=-1$ and substituting in (11) gives as the value of the integral:

$$[c(nl)]^2=\left(\frac{2}{\rho l}\right)^{2n-1}\frac{2l(l+n)!}{(l-n-1)!} \tag{13}$$

A second integral which will be needed is

$$A(n,l\lambda)=\int_0^\infty r^2\chi(nl)\chi(n-1\lambda)dr$$

which becomes, on substituting (6),

$$A(n,l\lambda)=\frac{(2n+2)!}{(l-n-1)!(\lambda-n)!}\left(\frac{\partial}{\partial z}\right)^{l-n-1}\left(\frac{\partial}{\partial y}\right)^{\lambda-n}\cdot \tag{14}$$
$$\frac{\left(z-\frac{1}{\rho l}\right)^{l+n}\left(y-\frac{1}{\rho l}\right)^{\lambda+n-1}}{(-z-y)^{2n+3}}$$

It has not been possible to effect any essential reduction of this expression, but its numerical value may be obtained from the expansion of (14):

$$A(n_1l\lambda)=(l+n)!(\lambda+n-1)!\sum_{\alpha=0}^{\lambda-n}\sum_{\beta=0}^{l-n-1}\frac{(2n+2+\alpha+\beta)!\left(-\frac{2}{\rho\lambda}\right)_{2n-1+\alpha}}{\alpha!(\lambda-n-\alpha)!(2n-1+\alpha)!} \tag{14a}$$
$$\frac{\left(-\frac{2}{\rho l}\right)^{2n+1+\alpha}}{\beta!(l-n-1-\beta)!(2n+1+\beta)!}$$

which is readily obtained by carrying out the differentiation.

The value of the constant B is to be determined in such a way that the matrices are Hermite. The author has shown (Ref. A) this is equivalent to the condition that

$$\int\int\int\psi(mnl)\psi(-mnl)dv=1 \tag{15}[6]$$

where the integral is to be extended over all space.
Since this integral may be separated into the product of three, and it is readily seen that

$$B=1/[\sqrt{2\tau}c(nl)D(mn)] \tag{16}$$

[6] The appearance of a negative sign in this formula is a consequence of the use of the function $\exp(im\phi)$ instead of the more usual sin or cos. The former notation has certain advantages for our purposes, and is permissible if the convention that $P_n^{-m}=P_n^m$ is agreed upon.

where $c\,(nl)$ has the value given by (7a) and (13), while

$$[D(mn)]^2=\int_{\pi/2}^{\pi/2}[P_n{}^m(\cos\theta)]^2\sin\theta d\theta=\frac{(n+m)!}{(n-m)!}\,\frac{2}{2n+1}$$

Certain formulas relative to the functions $P_n{}^m$ will also be needed[7]:

$$(2n+1)\cos\theta P_n{}^m=(n-m-1)P_{n+1}^{\,m}+(n-m)P_{n+1}^{\,m}$$

$$(2n+1)\sin\theta P_n{}^m=-(n-m+1)(n-m+2)P_{n+1}^{\,m}+(n+m-1)(n+m)P_{n-1}^{\,m-1}$$

$$=P_{n+1}^{\,m+1}-P_{n-1}^{\,m+1} \tag{18}$$

These functions also constitute an orthogonal set:

$$\int_{\pi/2}^{\pi/2}P_n{}^mP_\nu{}^m\sin\theta d\theta=0\;;\;n\neq\nu. \tag{19}$$

Calculation of the Matrices

Since three quantum numbers enter into the function ψ, the matrices will have six indices, three, mnl, for the initial state, and three, $\mu\nu\lambda$, for the final state of the atom. There will be a matrix for each of the rectangular coordinates x, y, and z. However, it will be more convenient not to calculate these matrices, but rather those corresponding to $x+iy$, $x-iy$ and z. These will be denoted by $R(mnl,\,\mu\nu\lambda)$, and $S(mnl,\,\mu\nu\lambda)$, and $Z(mnl,\,\mu\nu\lambda)$, respectively.

The calculation of R will be carried out in detail. It is defined by (Ref. A and II)

$$R(mnl,\mu\nu\lambda)=\int\int\int r^2(x+iy)\psi(mnl)\psi(\mu\nu\lambda)dv \tag{20}$$

where the integral is to be extended throughout all space. Since $x+iy=r\sin\theta\exp(i\phi)$, this integral is the product of three:

$$\frac{1}{2\pi}\int_0^{2\pi}\exp i(m+1-\mu)\phi d\phi$$

$$\frac{1}{D(mn)D(\mu\nu)}\int_{-\pi/2}^{+\pi/2}\sin^2\theta P_n{}^mP_\nu{}^\mu\,d\theta \tag{21}$$

and

$$\frac{1}{c(nl)c(\nu\lambda)}\int_0^\infty r^3\chi(nl)\chi(\nu\lambda)dr$$

The first integral is zero except when $\mu=m+1$ and then has the value unity. Hence the second need only be evaluated for $\mu=m+1$, and its

[7] I am indebted to Professor Epstein's notes for these formulas. They are due to C. Neumann, but the reference is not available.

value is readily obtained by multiplying the third of (18) by $\sin\theta\, P_\nu^{m+1}$ and integrating. From (19) it follows that it is zero except when $\nu = n \pm 1$ and from (17) that it is equal to

$$\frac{1}{2n+1}\,\frac{D(m+1\ n+1)}{D(mn)} \tag{22}$$

when $\nu = n+1$
and

$$\frac{-1}{2n+1}\,\frac{D(m+1\ n-1)}{D(mn)}$$

when $\nu = n-1$.

Hence the third need only be evaluated for $\nu = n \pm 1$ and is readily seen to be

$$\frac{A(n,l\lambda)}{c(nl)c(n-1,\lambda)} \tag{23}$$

when $\nu = n-1$

$$\frac{A(n+1,\lambda l)}{c(nl)c(n+1,\lambda)}$$

when $\nu = n+1$.

where A is the integral (14). The conclusion is that $R(mnl,\mu\nu\lambda)$ is zero except in the cases included in the formulae

$$\begin{aligned} R(mnl\,m+1\,n+1\,\lambda) &= \frac{1}{2n+1}\,\frac{D(m+1\,n+1)}{D(mn)}\,\frac{A(n,l\lambda)}{c(nl)c(n-1,\lambda)} \\ R(mnl\,m+1\,n-1\,\lambda) &= \frac{-1}{2n+1}\,\frac{D(m+1\,n-1)}{D(mn)}\,\frac{A(n+1,\lambda l)}{c(nl)c(n+1,\lambda)} \end{aligned} \tag{24}$$

The matrices S and Z may be computed in the same manner. Writing

$$J(nl\lambda) = \frac{A(n,l\lambda)}{c(nl)c(n-1,\lambda)} \tag{25}$$

and substituting for D its value, the result is that all the terms of the matrices are zero except the following, in which the substitution $k = n+\frac{1}{2}$ has been made:

$$R(mnl,m+1\,n+1\,\lambda) = \sqrt{\frac{(k+m+3/2)(k+m+\frac{1}{2})}{k(k+1)}}\cdot\tfrac{1}{2}J(k+\tfrac{1}{2},\lambda l)$$

$$R(mnl,m+1\,n-1\,\lambda) = -\sqrt{\frac{(k-m-\frac{1}{2})(k-m-3/2)}{k(k-1)}}\cdot\tfrac{1}{2}J(k-\tfrac{1}{2},l\lambda)$$

$$S(mnl,m-1\,n+1\,\lambda) = -\sqrt{\frac{(k-m+3/2)(k-m+\frac{1}{2})}{k(k+1)}}\cdot \tfrac{1}{2}J(k+\tfrac{1}{2},\lambda l) \qquad (26)$$

$$S(mnl,m-1\,n-1\,\lambda) = \sqrt{\frac{(k+m-\frac{1}{2})(k+m-3/2)}{k(k-1)}}\cdot \tfrac{1}{2}J(k-\tfrac{1}{2},l\lambda)$$

$$Z(mnl,m\,n+1\,\lambda) = \sqrt{\frac{(k+m+\frac{1}{2})(k-m+\frac{1}{2})}{k(k+1)}}\cdot \tfrac{1}{2}J(k+\tfrac{1}{2},\lambda l)$$

$$Z(mnl,m\,n-1\,\lambda) = \sqrt{\frac{(k+m-\frac{1}{2})(k-m-\frac{1}{2})}{k(k-1)}}\cdot \tfrac{1}{2}J(k-\tfrac{1}{2}),l\lambda)$$

Were the half quantum-numbers not used, the symmetry which is very evident in (27) would be quite obscured. This notation also brings out the Heisenberg "square," $\bar{k}^2 = k(k+1)$, which is so characteristic in the description of the Zeeman effect.

Discussion of the Matrices

According to the original definition of the matrices, each term of the matrix represents the amplitude of a partial oscillation of the electric moment of the atom. The matrix term $Z(mnl,\mu\nu\lambda)$, for example, represents the z-component of the amplitude of a partial oscillation of frequency $(1/h)(W_\lambda - W_l)$. Using a somewhat mixed terminology, it is the amplitude of the oscillation due to a transition from the state mnl to the state $\mu\nu\lambda$.

The formulas (26) therefore show that only those transitions in which m changes by ± 1 or 0 and k by ± 1 actually occur. When m does not change, only the matrix Z has a non-zero term, and the oscillation has therefore no x or y component—the light emitted is linearly polarized, in the usual sense of the term in spectroscopy. When m changes by 1 the R matrix has the non-vanishing term, and since R corresponds to $x+iy$, this represents emitted light which is circularly polarized. The change of m by -1 results in light which is also circularly polarized, but in the opposite sense.

These polarization rules correspond to those for the three components of the normal Zeeman effect, and a preliminary treatment of this effect shows that the separation is also given, in this theory, by the usual formula, the number m playing the usual rôle. There are still several fundamental questions to be answered before the discussion of this problem can be completed, however.

The quantum number k which changes only by ± 1 is evidently the azimuthal. This identification is rendered certain by a calculation of the

relativistic fine-structure (subject to the same uncertainty of theoretical interpretation, however, as the Zeeman effect). The additional term-value is

$$\Delta\nu=\frac{R\alpha^2}{l^4}\left\{\frac{l}{k}-\frac{3}{4}\right\},\quad R=\text{Rydberg constant},$$

which is identical in form with the expression given by the Sommerfeld theory. Since k in that theory takes on the values 1,2,3 . . . . , while in this theory it takes the values $\frac{1}{2},\frac{3}{2}$ . . . . , however, the levels will not coincide. This difference is apparently just that which is required by the theory of the rotating electron.[8]

Thus much for the identification of the quantum numbers. Since the intensity of the light emitted by an oscillating dipole is proportional to the square of the amplitude, the expressions (26) furnish the means of calculating this quantity. Since the atomic system under consideration is degenerate, the total intensity of the light of a given frequency emitted will be proportional to

$$I(l\lambda)=\sum_m\sum_k(\tfrac{1}{2}R^2+\tfrac{1}{2}S^2+Z^2)$$

$$m=-(k-\tfrac{1}{2})\to k-\tfrac{1}{2},\qquad k=\tfrac{1}{2}\to l-\tfrac{1}{2} \tag{28}$$

The factors $\frac{1}{2}$ appear because the R and S terms represent circularly polarized light.

An approximation to the relative intensity of the components of the relativistic fine structure may also be obtained. The intensity of the line corresponding to a transition from $\kappa\lambda$ to kl will be

$$I(kl,\kappa\lambda)=\sum_m(\tfrac{1}{2}R^2+\tfrac{1}{2}S^2+Z^2) \tag{29}$$

Carrying out the summation, it is found that

$$I(k-1\,l,k\lambda)=(k-\tfrac{1}{2})[J(k-\tfrac{1}{2}\lambda l)]^2$$
$$I(kl,k-1\,\lambda)=(k-\tfrac{1}{2})[J(k-\tfrac{1}{2}l\lambda)]^2$$

all others being zero. On calculating the quantities I for H_α, ($l=2$, $\lambda=3$), the intensities of the three components are given as proportional to

$$I(1/2\ \ 3,3/2\ \ 2)=\quad .879\rho^2$$
$$I(3/2\ \ 3,1/2\ \ 2)=\ \ 9.42\rho^2$$
$$I(5/2\ \ 3,3/2\ \ 2)=\ 45.2$$

These values are not in accordance with observation. According to experiments of W. V. Houston, the actual ratio of the intensities of the two brighter components is more nearly 8:10 than 2:10. For H_β

[8] Note added Oct. 23, 1926. Cf. Schroedinger, Ann. d. Physik **81**, 132 (1926).

$$I(1/2\ 4, 3/2\ 2) = .146\rho^2$$
$$I(3/2\ 4, 1/2\ 2) = 1.64\rho^2$$
$$I(5/2\ 4, 3/2\ 2) = 5.88\rho^2$$

whereas observation yields 9:10 for the ratio of the two brighter.

In how far this lack of agreement is to be laid to the general theory, and how far to the model on which the calculations are based, is not certain. The model is certainly incomplete, as is shown by the energy levels of the fine-structure predicted by this theory. The rotation of the electron, which is expected to remove this discrepancy, is also expected to predict a fourth component whose intensity is included in that of the fainter of the two components observed. It does not appear likely, however, that its intensity will be sufficient to account for all the difference.

This theory, so far as its determination of the energy levels and selection principles is concerned, is unimpeachable. It must be emphasized, however, that the identification of the matrix terms with dipole amplitudes constitutes an independent hypothesis.

It is a pleasant duty to acknowledge my indebtedness to Professors P. S. Epstein and H. Bateman for much valuable assistance, and to Mr. H. Hicks, who very kindly checked the numerical computations.

CALIFORNIA INSTITUTE OF TECHNOLOGY,
PASADENA, CALIFORNIA.
July 17, 1926.

THE CONTINUOUS SPECTRUM OF HYDROGEN

By W. H. Crew and E. O. Hulburt

Abstract

Effect of the source on the continuous spectrum of hydrogen.—The continuous spectrum of hydrogen is observed to be of similar character, although of differing intensity, in a number of sources, a Wood tube, an ordinary discharge tube, the separate striations of the positive column, the condensed spark in hydrogen at pressures above atmospheric, and in the water spark. It is of appreciable intensity near $H\alpha$, rises slowly to a maximum in the near ultra-violet and descends slowly in intensity from λ300 to 220$\mu\mu$.

Theory of the continuous spectrum of hydrogen.—Bohr's idea, which attributes a continuous spectrum near the Balmer lines to an electron plunging from an unquantized energy region to the second orbit, together with Wright's theory that such unquantization may exist from any given orbit outwards, is given statistical formulation on the assumption that the plunging electrons obey a Maxwellian law of distribution. A formula for the distribution of energy across the continuous spectrum is obtained which involves an unknown probability, a_n, that the atom exist through the nth orbit, the region beyond being unquantized. When a_n is evaluated roughly from general physical considerations the formula agrees qualitatively with the continuous spectra observed in the hydrogen stars and the laboratory sources. It is recognized that the theory is a simple type of the more general theory of retardation spectra.

THE continuous spectrum of hydrogen has been the subject of many investigations, for example those of Stark,[1] Gehrcke and Lau,[2] Carst,[3] Richardson and Tanaka,[4] Steubing,[5] Blackett and Franck,[6] Schüler and Wolfe,[7] and others. Nevertheless, its origin and exact character remain uncertain. Bohr has suggested that a continuous spectrum extending into the ultra-violet due to hydrogen atoms should begin sharply at the Balmer series limit, λ3646A. In simple terms Bohr's theory is that an electron may fall into the second quantum orbit of the atom nucleus with an unquantized energy $mv^2/2$ greater than that necessary to emit the limiting line of the Balmer series. Thus, since $mv^2/2$ may increase continuously from zero, frequencies extending continuously from the series limit into the ultra-violet would be radiated. A continuous spectrum of about this sort occurs at the limit of the principal series of sodium

[1] Stark, Ann. d. Physik **52**, 221 (1917).
[2] Gehrke and Lau, Preuss. Akad. Wiss Berlin. Ber. **24**, 242 (1923).
[3] Carst, Ann. d. Physik **75**, 665 (1924).
[4] Richardson and Tanaka, Proc. Roy. Soc. **106**, 640 (1924).
[5] Steubing, Zeits. f. Physik **32**, 159 (1925).
[6] Blackett and Franck, Zeits. f. Physik **34**, 389 (1925).
[7] Schüler and Wolfe, Zeits. f. Physik **33**, 42 (1925).

and of potassium[8,9,10]; in these instances the continuous spectrum and the series lines were observed in absorption. In hydrogen a continuous spectrum exists in the region of the Balmer lines, but instead of originating at the Balmer limit it begins always on the red side of the Balmer limit. Therefore the simple theory of Bohr, which attributes a continuous spectrum to the hydrogen atom, if it is to be retained at all, requires modification. Such a modification is developed in the following pages. It follows in the main certain ideas sketched out very briefly by Wright,[11] but departs from those ideas at certain points. Spectrograms of the continuous spectrum of hydrogen have been obtained under a variety of experimental conditions and are discussed in the light of the theoretical formulas.

THEORETICAL

The frequency ν_n of a Balmer line is given by the relation

$$h\nu_n = W_n - W_2 \tag{1}$$

where W_n and W_2 are the negative energies of the electron in the nth and the second quantum orbits, respectively. We assume with Wright[11] that an atom may possess quantum orbits out through the nth only. The orbits beyond the nth are broken off, so to speak, and the region is unquantized. It follows that an electron can fall into the second orbit from the nth with an energy greater than its orbital energy in the nth orbit by an amount $mv^2/2$, which may vary continuously from zero to infinity. Radiation of frequency ν will be emitted, where $h\nu = W_n + mv^2/2 - W_2$. This together with (1) yields

$$h\nu = h\nu_n + mv^2/2 \quad . \tag{2}$$

As $mv^2/2$ takes values from zero to infinity, ν maps out a continuous spectrum, either of emission or absorption, associated with each Balmer line, which begins at the line and extends to the shorter waves.

The distribution of energy across the continuous spectrum is calculated by statistical methods. In an assemblage of atoms of luminous hydrogen we may suppose that all types of atoms will be present in greater or less degree, excited to various energy levels, some with only a few quantized orbits and others with a greater number. The complete radiation which is emitted, or absorbed, as in the case of a bright back-

[8] Wood, Astrophys. J. **29**, 97 (1909).
[9] Bevan, Proc. Roy. Soc. **85**, 54 (1910).
[10] Holtsmark, Phys. Zeits. **20**, 88 (1919).
[11] Wright, Nature **109**, 810 (1922); see also Nicholson, Roy. Ast. Soc. Monthly Notices **85**, 253 (1925).

ground spectrum transmitted through the hydrogen, will be made up of the contributions of the Balmer lines and the continuous spectra from the various types of atoms. It is assumed that the hydrogen gas is in thermo-dynamic equilibrium and that the distribution of energy among the free electrons may be calculated from the usual formula of the kinetic theory. The number of electrons of energy $mv^2/2$ is then proportional to

$$\tfrac{1}{2}mv^2\epsilon^{-mv^2/2KT} \tag{3}$$

where T is the absolute temperature and K is the molecular gas constant, 1.372×10^{-16} ergs per degree Kelvin. We shall assume that (3) dictates the distribution of energy among the electrons which plunge into the second orbit of the hydrogen atoms giving rise to radiations. The intensity I_ν' of radiation of frequency ν is also proportional to expression (3), and upon introducing (2) we obtain

$$I_\nu' = a_n h(\nu-\nu_n)\epsilon^{-h(\nu-\nu_n)/KT}. \tag{4}$$

a_n is constant with respect to ν, but in general varies with n. Eq. (4) gives the intensity across the continuous spectrum for each value of n. We note that the curves of I_ν' plotted against wave-length descend to zero at each Balmer line; see, for example, Fig. 1. The complete continuous

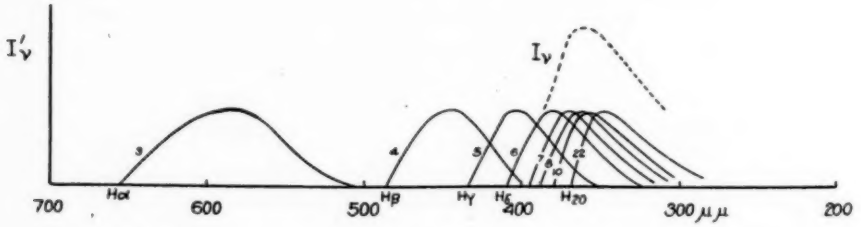

Fig. 1. Theoretical curves of I_ν' and I_ν for hydrogen at 2500°K, as in the reversing layers of the stars.

spectrum is the sum of the separate spectra, and the resultant intensity I_ν of radiation ν of the complete spectrum is

$$I_\nu = \sum_{n=2}^{n=\infty} a_n h(\nu-\nu_n)\epsilon^{-h(\nu-\nu_n)/KT}. \tag{5}$$

The relative intensity of the separate continuous spectra of the summation of (5) is given by a_n. This quantity is equal to the product of two factors a_n' and a_n'', a_n' being the probability of the existence of orbits out to and including the nth, and a_n'' the probability of the non-existence of orbits beyond the nth. (We must remember that the geometrical manner of speaking is perhaps only figurative, what is really in mind

is an interplay of energy transfers.) It would seem possible to evaluate a_n' and a_n'' from the observed intensities of the Balmer lines. An attempt to do this, however, by the use of Einstein's probability coefficients after the manner of Milne[12] was unsuccessful because of a welter of unknown quantities and uncertainties of assumption. At any rate, a_n' obviously decreases rapidly with n. a_n'' increases rapidly with n, for the chance that an atom exists with all its orbits removed beyond the third, for example, is certainly small, whereas an atom with orbits absent beyond the fifteenth, say, may exist more readily. The product $a_n' \times a_n''$, or a_n, may from general physical considerations be expected to be small for small values of n, larger for intermediate values, and smaller again for high values of n.

The theory of Wright is the same as the foregoing theory in that the orbits below the nth are assumed to be quantized and those above unquantized, but differs in respect to the nth orbit. This is taken to be partially quantized. As a result the I_ν' curves will not drop to zero at each Balmer line but will extend to the red of the line. The experimental evidence may be represented equally well by either theory. As a matter of fact, it is hardly to be expected that either of these views is entirely correct. We recognize them to be special cases of the general retardation spectra which may occur when an electron loses energy in passing near an atom nucleus. And, quoting Sommerfeld,[13] "Everything still remains to be done for the proper theory of this retardation spectrum." There may be, as others have pointed out (for example, Stark[1]) more than one type of continuous spectrum emitted by luminous hydrogen, although the present experiments give no certain indication of this, one associated with the atoms, perhaps, one with the H_2 molecules, etc. These possibilities are included in a general way in the idea of the retardation spectrum. For, if the spectrum arises from the interaction of an electron and a hydrogen nucleus, the nucleus may be that of a free (i.e., undisturbed) atom, or that of an atom disturbed by surrounding atoms or ions which may or may not be attached to it sufficiently firmly to form molecules, or that of an atom disturbed in some other way. Indeed, the conception of the retardation spectrum is such a general one as to be almost unsatisfactory. It will now be apparent that although we have spoken of atoms in deriving the formulas, we have not meant necessarily the free partcles of a monatomic gas; the atom deprived of its outer orbits, as we put it, may very well be part of a molecule, or it just as well may not be. Therefore the explicit use of the Balmer orbits must be

[12] Milne, Phil. Mag. **47**, 209 (1924).

[13] Sommerfeld, Atomic Structure and Spectral Lines, 451 (1922).

regarded as illustrative, and the formulas as first, and perhaps distant, approximations.

Stellar Spectra

In the spectra of the stars and nebulae[14] which exhibit a well developed Balmer series, usually of absorption, a continuous spectrum is seen near the series limit. This appears to have a maximum of intensity in the region of the limit and to extend a short way to either side, 10 to 200A to the red of the limit and possibly 400A, or less, to the short wave side. With $T=2500°K$ the curves of I_ν' against λ, where λ is the wave-length corresponding to the frequency ν, were calculated from (4) for each value of n and are plotted in the heavy line curves of Fig. 1. The value of n is written alongside each curve in the figure; for $n=3$, the curve corresponds to H_α, for $n=12$, to H_{10}, etc. The curve for $n=2$ is not drawn; its maximum is at $\lambda 5.7 6\mu$, and it makes a negligible contribution in the region of the spectrum under consideration. On the scale of Fig. 1 H_{30} is indistinguishable from H_{20}. The maximum ordinates of all the curves are made equal, this means that a_n was the same for all values of n. The final intensity curve I_ν, from (5), is obtained by adding the ordinates of the I_ν' curves of Fig. 1, assigning to each curve its value of a_n. In order to make the I_ν curve, sketched in the dotted line of Fig. 1, agree with the observed continuous spectra of the hydrogen stars, a_n must be small for the earlier and later values of n; so that only the I_ν' curves for n from, say, 9 to 22 make appreciable contributions to the I_ν curve. This type of variation of a_n with n is in reasonable accord with the physical notions of low temperatures and pressures in the reversing atmospheres of the stars and with the low decrement of the Balmer line intensities.

Experiments

A long hydrogen tube constructed after the manner of Wood[15] with the light coming end-on through a quartz window from the central portion only was operated in the "black stage," i.e., the Balmer lines strong and the molecular lines relatively weak. Moist hydrogen was introduced into the tube through a slender glass capillary and was excited by a 10 kv, 1 kw, 500 cycle transformer. The continuous spectrum always appeared in the spectrum of this tube. In general as the conditions of pressure, water vapor, current, etc., in the tube were changed so as to increase the purity of the atomic lines the continuous spectrum became

[14] Hartmann, Phys. Zeits. **18**, 429 (1917); see also Wright, loc. cit. 11, and Ch'ing-Sung Yü, Lick Observatory Bulletin, No. 375, 1926.

[15] Wood, Proc. Roy. Soc. **97**, 455 (1920).

weaker throughout its entire extent. With exposures sufficiently long to bring out sixteen of the Balmer lines the continuous spectrum began somewhere near H_α and extended smoothly to the ultra-violet limit of observation $\lambda 230\mu\mu$. None of these spectrograms are reproduced here.

With dry hydrogen in the tube at a pressure of 6 to 8 mm of mercury, the continuous spectrum was of the same general character as that of the Wood tube. It was, however, vastly more intense and could be followed visually into the red easily as far as H_α, and perhaps beyond. The spectrum is shown in the two strips *a* and *b* of Fig. 2, for the longer and shorter wave-length regions, respectively. On strip *b* is an iron com-

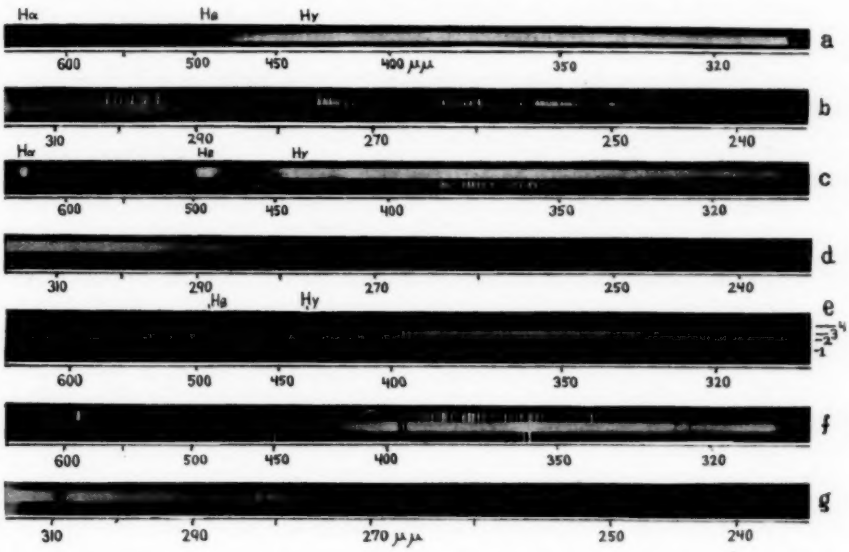

Fig. 2. Continuous spectrum of hydrogen from various sources; *a* and *b*, ordinary discharge tube, pressure 8 mm of mercury; *c* and *d*, condensed spark in hydrogen at one and a half atmospheres; *e*, striations of the positive column; *f* and *g*, condensed spark between aluminum terminals in water.

parison spectrum. As seen in the visual spectrograph the continuous spectrum fell off to the red above H_β much less slowly than strip *a* would indicate; the rapid decline there is due to the insensitiveness of the panchromatic plate in the yellow-green. The slow decline in intensity towards the ultraviolet in the region $\lambda 3000$ to 2300A of strip *b* is really less rapid than it appears to be, for the dispersion of the spectrograph is increasing to the shorter wave-lengths. We may conclude that the continuous spectrum began in the red, rose gradually to a mild maximum of intensity in the near ultra-violet, and then fell off slowly in the region

[18] Lewis, Phys. Rev. **16**, 367 (1920).

λ3000 to 2300A. We may supplement this with a statement from Lewis[18] that the spectrum falls to a very low intensity at about λ1750A.

The spectrum of strips *a* and *b*, Fig. 2, is the spectrum of the "ordinary" hydrogen tube. Such a tube is a relatively weak source of visible light, but a very powerful source of ultra-violet light. When the conditions in in the tube are changed to bring out the Balmer spectrum the reverse is true, the tube gives a very brilliant visible light and but little ultra-violet light. Sensible evidence of this is obtained by sniffing the ozone in front of the tube.

In applying the formulas to the vacuum tube continuous spectra a temperature of 20,000°K is assumed. The curves from (4) are given in Fig. 3 plotted with a_n constant, i.e., maximum ordinates equal. The maximum of the I_ν' curve for H_α ($n=3$) is at λ343$\mu\mu$. If a temperature 10,000° had been chosen the maximum would have been at λ450$\mu\mu$, and the curves would differ but little from those of Fig. 3. The I_ν' curve for $n=2$, which is a maximum at λ716$\mu\mu$, drops off slowly across the visible and ultra-violet spectrum. It refers to the atom stripped of all its orbits down to the second. To obtain the I_ν curve, sketched in the dotted line of Fig. 3, in agreement with the vacuum tube continuous spectrum, we

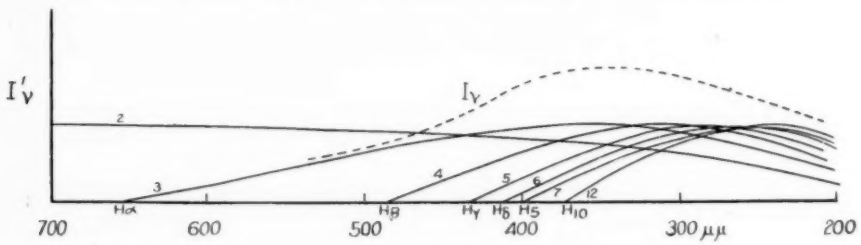

Fig. 3. Theoretical curves of I_ν' and I_ν for hydrogen at 20,000°K, as in a discharge tube.

must give greater importance to a_n for the earlier values of n. This is in keeping with the relatively high temperatures and pressures of the vacuum tube and the rapid decrease of the Balmer line intensities. Whether the I_ν' curve for $n=2$ should be considered at all is an open question. If the present view is correct one could perhaps decide this by observing whether the continuous spectrum extended to the red of H_α. This was attempted many times visually and photographically, with the result that a faint luminosity to the red of H_α was observed, so faint, however, that it may have been due to scattered light in the spectrograph. In this connection it may be mentioned that the ideas of this paper extended to the Lyman and infra-red levels of atomic hydrogen would lead to the possibility of continuous radiation, probably weak, veiling the visible and ultra-violet regions of the spectrum.

We may now pass to an examination of the continuous spectrum from hydrogen at higher pressures. A Pyrex bulb with a quartz window was fitted with two aluminum electrodes about 5 cm apart and was filled with dry hydrogen at a pressure of about one and a half atmospheres. The quartz window was arranged to view only the central portion of the discharge and not the electrodes. The spectrum of vigorous condensed discharges, about 7 amp., through the hydrogen was photographed and is shown in strips *c* and *d*, Fig. 2, for the longer and shorter wave-length regions respectively. In strip *c* the Balmer lines are greatly broadened, due to the Stark effect,[17] and soon fuse together in the march of the series to form a continuous spectrum, Hγ being the last line to appear separated from its neighbors. At the same time a continuous radiation extends throughout the entire spectrum. This has much the same characteristics as those of the lower pressure hydrogen of strips *a* and *b*, except that it declines more rapidly in intensity in the ultra-violet. Strip *d* is perhaps three times as strong as *b* at λ3100 and somewhat weaker than *b* at λ2400. Its maximum of intensity is apparently somewhere in the near ultra-violet. The molecular lines do not occur at all in this spectrum, and the more prominent aluminum lines but faintly. The spectrum of the high pressure hydrogen saturated with mercury vapor was much the same as that of strips *c* and *d* with the addition, of course, of the mercury lines. The line 2536A was reversed and broadened. There was no diminution of the continuous spectrum below λ2536A corresponding to the first resonance potential of mercury, as might be expected from the experiments of Schüler and Wolfe.[7]

For the hydrogen at the greater pressures, and possibly greater temperatures, the higher orbits may be expected to be even more unstable than for the lower pressure hydrogen of strips *a* and *b*, Fig. 2. Consequently, a_n for $n=2, 3, 4$, etc., must be given even greater weight over the later values than was done for the lower pressure hydrogen. This will yield an I_ν curve which drops off faster in the ultra-violet than the curve of Fig. 3, in entire conformity with the spectrum of strip *d*, Fig. 2.

An experiment by Horton and Davis[18] in which a continuous spectrum was obtained entirely free from atomic lines deserves a few remarks. They observed that hydrogen at a moderate pressure, less than 1 mm of mercury, excited by electrons of energy less than 15 volts became suffused with a blue glow which yielded a continuous spectrum with no traces of lines of the molecular or atomic spectra. The continuous

[17] Hulburt, Phys. Rev. **21**, 24 (1923).
[18] Horton and Davis, Phil. Mag. **46**, 872 (1923).

spectrum, although fading out towards the red, definitely extended to the long wave side of $\lambda 478\mu\mu$. This is the wave-length corresponding to 2.4 volts, which was the dissociation potential ascribed to H_2. It was therefore suggested that the continuous spectrum, in part at any rate, might possibly be attributed to the formation of aggregates such as H_3.

In the present instance we have obtained this low voltage spectrum in a slightly different way. A small straight glass discharge tube 15 cms long and 7 mm inside diameter with aluminum electrodes at either end was excited with 500 cycle alternating current rectified by a kenotron. (The rectified current was used merely because of convenience, direct current would have served as well.) The tube was connected permanently to a large bottle of about 10 liters capacity, in order to maintain the pressure steady, and the whole system was filled with dry hydrogen. At a pressure of about 1 mm of mercury the first striation of the positive column, the striation next to the Faraday dark space, appeared a vivid blue, whereas the other striations were pinker or whiter. The blue striation was usually narrower than its neighbors. The image of this tube was focussed broadside on the slit of the spectrograph, so that the spectra of several striations could be observed simultaneously. These are shown in strip *e*, Fig. 2. Region 1 of the strip is the Faraday dark space, 2 the blue striation, 3 the second striation, and so on. It is seen (as well as the reproduction will permit) that the spectrum of the blue striation is a continuous spectrum free from the Balmer and molecular lines, whereas the other striations of the positive column contain all three spectra. The continuous spectrum of the blue striation is evidently the same as that in the low voltage experiment of Horton and Davis. For Bramley[19] has found that at pressures of the order of 1 mm of mercury the electrons in the striation nearest the cathode have velocities of about 10 to 15 volts. Furthermore, at these pressures Smyth and Brasefield[20] in a positive ray analysis of the ions in the positive column of hydrogen have observed a large proportion of H_3^+ ions.

We regard this low voltage continuous spectrum as a retardation spectrum of much the same type as the other vacuum tube continuous spectra of Fig. 2. The strong concentration of H_3^+ ions in the regions where the spectrum arises is taken to mean that in these regions partially or completely unquantized atomic nuclei exist. An experiment in keeping with these general ideas is that of Lemon[21] who observed a continuous spectrum of unusual intensity from hydrogen excited by a one ampere current

[19] Bramley, Phys. Rev. **26**, 794 (1925).
[20] Smyth and Brasefield, Phys. Rev. **27**, 514(A) (1926).

of electrons from a hot cathode at 100 volts. These violent conditions are exactly suitable for the removal of the outer quantum orbits (always speaking geometrically) and therefore a strong retardation spectrum would be anticipated.

The spectrum of the condensed spark between aluminum terminals in hydrogen at pressures above atmospheric, as in strips *c* and *d*, Fig. 2, is remarkably similar to the spectrum of the condensed spark between aluminum terminals under water[22] shown in strips *f* and *g*, Fig. 2. The type of electrical excitation and the current, 7 amp., were the same in each case. This suggests that the continuous spectrum of the water spark is a retardation spectrum arising from electrons plunging into or near hydrogen nuclei. This is supported by the fact that the character of the continuous spectra from the water spark is unaffected by the kind of metal used for the electrodes. It seems probable that the hydrogen nuclei are more important to the production of the continuous spectrum than other atoms. For a spark between aluminum terminals under carbon tetrachloride was found to yield a much weaker continuous spectrum, although otherwise like that in water. The carbon tetrachloride was the commercial material and may have contained hydrogen in the impurities; also, no effort was made to rid the electrodes of hydrogen. Further, the spectrum of the condensed spark between aluminum terminals in dry air at atmospheric pressure,under the same conditions as in hydrogen, possessed a much fainter background continuous spectrum than that from hydrogen. The fact that the continuous spectrum appears strongest in hydrogen, next strongest in helium, and less strong in other elements (the meager experimental data allow no certain estimates farther into the periodic table) suggests that the intensity of the continuous spectrum is a decreasing function of the mass of the atomic nucleus.

In conclusion we may call attention to the uses of the various sources of continuous spectra for investigations in the ultra-violet. The most intense source is the spark in water or in hydrogen at a high pressure, and is useful for qualitative experiments such as the observation of absorption lines, etc. It is not at all difficult to arrange and operate. Like any spark it is unsteady and therefore unsuited for quantitative spectrophotometry. Aluminum or copper are convenient metals for the electrodes of the water spark, the aluminum preferably in the form of duralumin and the copper in phosphor bronze, for these alloys splinter away less rapidly than the pure metals. As a source sufficiently steady for quantitative measure-

[21] Lemon, Nature **113**, 127 (1924).
[22] Hulburt, Phys. Rev. **24**, 129 (1924).

ments there seems to be nothing better than the ordinary hydrogen tube, 5 to 10 mm in diameter and at a pressure of 2 to 10 mm of mercury, used end-on. Its spectrum is very uniform throughout the entire region from λ500 to 200$\mu\mu$, which is a great advantage. The most serious disadvantage is the weakness of its spectrum; this, however, may be overcome to some extent by allowing the tube to absorb considerable electrical energy.

NAVAL RESEARCH LABORATORY,
WASHINGTON, D. C.,
July 22, 1926.

THE IONIZATION OF ATOMS BY ELECTRON IMPACT

By Ernest O. Lawrence*

Abstract

A method of high precision for the measurement of critical potentials. Precision in critical potential measurements in the past has been seriously limited by the lack of homogeneity in velocities of the electrons. This source of error has been eliminated by separating out magnetically electrons of definite velocities. The electron beams used in the present experiments were not characterized by great homogeneity in velocities but by *sharp upper limits* to their velocity distributions. Critical potentials were measured as the differences between two retarding potentials—the smallest retarding potential preventing the entrance of the electrons into the Faraday cylinder type of ionization chamber and the largest retarding potential for which the effect under investigation is observed—thereby eliminating errors due to contact electromotive forces.

Critical potentials in mercury vapor. The following critical potentials associated with ionization of mercury vapor have been observed: 10.40, 10.60, 11.29, 11.70 and 12.06 volts, respectively. The first is identified with simple ionization of the mercury atom while the ultraionization potentials are regarded as most probably due to simultaneous ionization and removal of another electron to a higher energy level in the atom. It is also suggested that the new critical potentials may be identified with band spectra data.

Ionization probabilities. Analysis of the data indicates very strikingly that each type of inelastic impact involving ionization has a *maximum* probability of production when the impacting electron has just enough energy to carry through the process, the law governing the probability being of the form,

$$P(e) = P_{e_0} \epsilon^{-10(e-e_0)/e_0}$$

where e_0 is the associated critical potential and e is the energy of the impacting electron. The constants P_{e_0} for the several types of impacts are as follows:

e_0	10.40	10.60	11.29	11.70
Pe_0	0.25	1.0	1.4	1.15

A correspondence principle.—The above law governing the probability of ionization by electrons is identical with the corresponding probability law governing the photo-electric ionization of caesium vapor observed by Mohler, Foote and Chenault. This fact has led to the following generalization: Light quanta and electrons obey the same general laws in processes involving ionization of atoms and molecules. In particular, the probability of atomic ionization of a certain type by a light quantum is the same function of its energy—excepting for constants—as the probability of the corresponding electron inelastic impact. The generalization correlates the author's results on the photo-electric ionization of potassium vapor, the mentioned results in caesium vapor, the observations of recent investigators on ionization probabilities by low velocity electrons and the results recorded in this paper. Furthermore, since ionization by high velocity electrons is, in the main, a process that is described on the basis of classical laws—conservation of energy and momentum—the general

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correspondence here suggested indicates that there is a similar ionization process by light quanta of great energy. *The Compton Effect bears out this implication.*

The ratio e/h. Assuming the first critical potential to be associated with the series limit frequency ν by the relation $Ve=h\nu$, the ratio e/h is determined to be 7.28×10^{16} with a probable error of 0.2 percent. In conjunction with the Bohr theory of the Rydberg constant and known spectroscopic data this leads to values for e and h individually in agreement with the accepted values.

Introduction

THERE is evidence[1] that rapidly distilling potassium vapor is in a diatomic molecular form having an ionization potential of 4.7 volts, that is, 0.4 volt greater than the atomic value observed in the vapor when in equilibrium. During the course of some experiments designed to test this point it became clear that the methods[2] usually employed in critical potential measurements were *not* able to yield results of sufficient precision. The factors which have mitigated against precision are well recognized but it may not be amiss to emphasize the most troublesome source of errors, namely, the initial distribution of velocities of the electrons from the thermionic cathode. This distribution of velocities prevents sharp "breaks" in critical potential curves and, indeed, the positions of the apparent breaks are dependent on the sensitivity of the measuring devices. This latter condition has in many cases been disregarded, perhaps because of its rather deceptive nature, although it is clear that an apparent curve break involving a Maxwellian velocity distribution may be shifted more than 0.5 volt when the scale of plotting is altered by a factor of 10.

Accordingly, a new method and technique has been developed which, as well as making possible highly accurate critical potential determinations, has produced important information on probabilities of ionization by low velocity electrons.

The Method and Experimental Arrangement

The method centers on separating out electrons of definite velocities from a thermionic source by means of a suitable series of diaphragms and magnetic field. In the original plan of the apparatus the design was such that it was thought possible to produce a beam of electrons all moving within 1 percent of a mean velocity and of a magnitude suitable for critical potential work. The initial experiments showed, however, that space charge phenomena prevented the attainment of this objective and

[1] Lawrence, Phil. Mag. **1**, 345 (1925).

[2] A complete resumé of critical potential methods and results is contained in a bulletin of the National Research Council on "Critical Potentials," by K. T. Compton and F. L. Mohler.

the desired degree of precision was realized by producing a beam having a wider band of velocities with a *sharp upper limit.* These velocities were readily altered to any set of values simply by the superposition of additional accelerating voltages.

Figs. 1 and 2 depict the arrangement of the apparatus. Electrons are accelerated from an oxide coated filament F of special design to a grid G and after retardation pass through the first slit of the analyzing chamber AC. A portion of the entering electron stream is deflected through the circle of slits by the magnetic field, emerging into a Faraday cylinder type of ionization chamber I where they are absorbed. An insulated wire A and grid B were used to detect resulting ionization in the cylinder. The procedure was then to find the distribution of velocities of the electrons entering the Faraday cylinder by retarding potential measurements and the ionization therein as a function of its potential. It is clear that a critical potential is determined as the difference between the minimum retarding voltage that must be applied to the chamber to prevent the entrance of electrons and the maximum retarding voltage for which there is observed the phenomenon under investigation. The components of the arrangement are discussed below.

Thermionic source. One of the major difficulties centered around obtaining currents through the slits of the analyzing chamber large enough to produce measurable ionization. An ordinary filament source although capable of giving a copious supply of electrons is not alone effective because with low accelerating voltages the mutual repulsions of the electrons prohibit large currents through the narrow slits. The difficulty was overcome by inserting a grid G between the filament and first slit. The electrons were accelerated through this grid by potentials of the order of 200 volts and subsequently retarded to the low value desired when passing through the first slit. Because of the presence of vapor in the region, the electrons when traveling with the higher velocities produced a large number of positive ions. The presence of such a positive ion sheath in the neighborhood of the filament and slit permitted sufficiently large currents to pass into the analyzing chamber. Since the same vapor density existed in the analyzing chamber and the velocities of the electrons traversing the slits were in general greater than the ionization potential of the vapor, a positive space charge existed also along the path of the beam. This fact contributed to modify the magnitude of the current favorably and tended to widen the band of velocities emerging from the final slit.

The inserted side-section of the filament (Fig. 1) shows that the magnetic field due to the filament heating current was very small. The filament mounting was of tungsten so that a further distortion of the field due to the presence of magnetic materials was eliminated.

Analyzing chamber. Fig. 1 shows to scale the design of the analyzing chamber with the relative positions and sizes of the diaphragms. The electrons entered the chamber from the thermionic source through a slit .013 cm wide and 1 cm in length and emerged through a .02 cm slit. The unusually large number of diaphragms reduced to a minimum

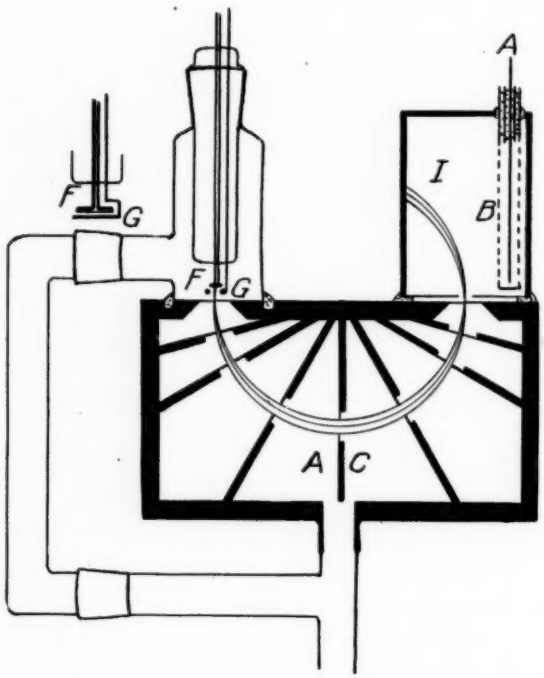

Fig. 1. Diagram of analyzing chamber.

spurious effects arising from reflections of electrons. Electric fields due to contact electromotive forces were eliminated by constructing the entire chamber from a single piece of brass material. The distance between the initial and final slits was 10 cms so that emergent electrons traversed circles of 5 cms radii. The proper widths of intervening slits relative to the first and last were carefully computed and adjusted with an accuracy of at least 0.1 percent. The brass chamber AC was assembled mechanically tight while sealing wax served to make the system vacuum tight. Fig. 1 shows the glass tube containing the thermionic source sealed

on with wax to the analyzing chamber. An arrangement of ground joints in the leads to the diffusion pumps permitted the ready removal of the glass enclosure when alterations were made.

Magnetic system. Fig. 2 indicates the arrangement of the magnetic system. The analyzing chamber was mounted on the axis of a pair of Helmholtz coils so that the slits were on a circle with center on the axis. Immediately above the chamber was mounted an earth inductor which served to show when the combined magnetic field due to the coils and the earth's field was in a direction parallel to this axis. With the expectation that accurate independent estimates of the electron velocities would be made from precise determinations of the deflecting magnetic field, the Helmholtz coils were constructed with greatest care. Machined brass castings formed beds (60 cm diam.) for 182 turns of No. 22 silk and enameled covered wire. The high degree of uniformity of the magnetic field was undoubtedly desirable for obtaining the large electron currents through the circle of narrow slits but the velocities of the emergent electrons were not uniquely dependent on the magnetic field as space charge played an important and variable role.

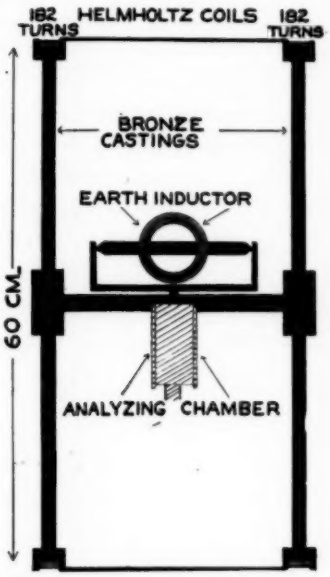

Fig. 2. Arrangement of Helmholtz coils.

Ionization chamber. A Faraday cylinder I 8.9 cm in length, 5.1 cm wide with a slit opening of 1.2 cm by 0.3 cm served as the chamber in which the ionization was measured. Several fine wires crossed the opening so that to all practical purposes the whole interior was at the same potential. The positive ions formed in the chamber were accelerated by a small voltage to a brass grid B which surrounded the brass wire collector A. The portion passing through was drawn to A by a much larger accelerating potential thereby preventing any electrons reaching the wire collector. Clearly this arrangement affected the velocities of the electrons entering the cylinder very little and minimized spurious photoelectric effects.

The electron current to the ionization chamber was measured by an electrometer connected across India ink resistances in the usual manner

while the positive ions were measured by the rate of deflection of a new type of electrometer designed by Professor W. F. G. Swann. This electrometer combined maximum sensitivity with convenient operation, ordinarily being used at a sensitivity of 8000 div. per volt.

Potentiometer. The potential of the ionization chamber relative to the final slit of the analyzing chamber was accurately maintained (exclusive of contact e.m.f.s) at any desired value by a potentiometer arrangement. A Leeds and Northrup potentiometer with Eppley standard cell accurately fixed a current of 1 milliampere flowing through a series of resistances from which potential differences were tapped. The whole system was calibrated by a Wolff potentiometer and a standard cell whose e.m.f. was known with a precision well within requirements. Thus, the applied potentials were known to within approximately 0.05 percent.

Vacuum. Mercury diffusion pumps kept pressures as registered on a McLeod gauge below a measurable value. However, in the present experiments mercury vapor was present throughout the system at a pressure corresponding to room temperature (about 27°C).

Errors

This experimental method presents several possible sources of errors and extended preliminary investigations and precautions have been taken to minimize their magnitude, as the following discussion indicates.

Contact electromotive forces. The most important source of error is concerned with contact electromotive forces of the various metal surfaces. It is important not only because of its magnitude but because of its elusiveness, a deceptive characteristic admirably illustrated in the present research. When the apparatus was first assembled consistent and reproducible results were obtained while later it was found that the experimentally observed values for the various critical potentials were assuming consistently higher values. In the course of a month the values were about 0.2 volt higher than originally and so they persisted in spite of all attempts to find the agency that had caused the change. Clearly, since a critical potential was measured as a *difference* between two potentials applied to the ionization chamber, presumably the effects of contact electromotive forces between the chamber and the slit from which the electrons issued out of the analyzing chamber would be canceled out. However, such an assumption was valid only in case the *inside* surface of the chamber had the same contact e.m.f. as the *external* surface adjacent to the analyzing chamber. This is an interesting point for it involves a fact not generally recognized, viz., that a contact e.m.f. may vary considerably over the surface of a single piece of metal, though

seemingly the metal is quite homogeneous. In view of this fact one readily recognizes that—unless the slit of the ionization chamber is designed properly with respect to the slit of the analyzing chamber—the present method may not eliminate entirely the effects of contact e.m.f.s; for when retarding potentials are applied to prevent the entrance of the electrons into the ionization chamber, the electrons proceed only to a region between the ionization chamber and the analyzing chamber and are in a potential field involving the applied retarding potential and the contact e.m.f. due to the immediately adjacent surfaces, viz., the *outside* surfaces of the analyzing and ionization chambers, while when retarding potentials are applied to merely slow down the electrons when traversing the interior of the ionization chamber the retarding potentials experienced by the electrons are made up of the applied potentials and the contact e.m.f. between the *inside* of the chamber and the final slit of the analyzing chamber. With these considerations in view, the slit of the ionization chamber was widened (the final dimensions are given in a preceding paragraph) and placed very close to the analyzing chamber (about 1 mm) so that the outside surface of the ionization chamber presumably contributed negligible contact e.m.f. fields in the region through which the electron beam passed into the ionization chamber. As a further precaution all metal surfaces were carefully sandpapered to reduce contact e.m.f.s to as nearly uniform values as possible. This done, consistent data were obtained which are regarded as highly probably free of appreciable systematic errors of this sort.

Diffusion of positive ions. There is evidence that there were some positive ions diffusing into the ionization chamber from external regions and it is not known to what extent the phenomenon has affected the observed results. In all cases, electron beams emerging from the analyzing chamber were used having velocities above the ionization potential (this was necessary to get large enough currents) so that there were positive ions present outside the ionization chamber which were drawn into the chamber by the retarding potentials applied in the experiments. Since, however, the results observed were not affected appreciably when the velocity of the electron beam issuing from the analyzing chamber was varied from about 11.0 to 15.0 volts, it is reasonable to conclude that the diffusion of positive ions from the outside did not contribute to the observed effects.

Details of technique. A large number of factors determined the nature of the electron beam and the ionization observed—such as the magnetic field, temperature of filament, various accelerating and retarding potentials, vapor pressure, etc.—and a requirement for trustworthy results

was therefore constancy of all these elements. By maintaining a constant temperature in the room and using adequate individual storage battery sources of current and potential it was possible to keep conditions constant for extended periods. This constancy was always checked by taking data in the order, first an observation of the electron velocity distribution, next observation of the ionization as a function of various retarding potentials and lastly a redetermination of the velocity distribution.

India ink resistances used to measure the electron currents became polarized to a certain extent and possible modification of observations by such a phenomenon was investigated by reversal of the direction of the polarization. In this way it was shown that the observed currents

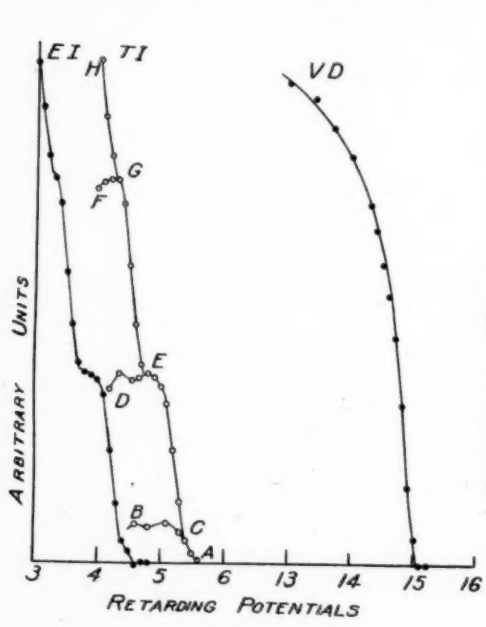

Fig. 3

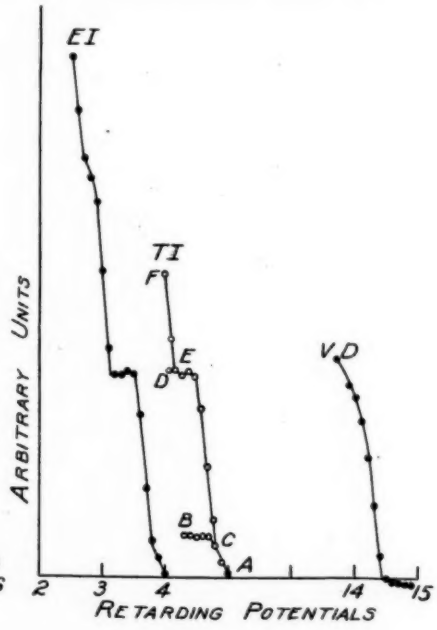

Fig. 4

Fig. 3. The ordinates of *VD* are the electron currents entering the ionization chamber corresponding to retarding potentials represented by the abscissas. (Maximum electron current about 10^{-11} amp.) The ordinates of *EI* record relative values of the ionization as a function of retarding potentials given by the abscissas. Curve *TI* is an ionization curve—abscissas shifted 1 v.—theoretically calculated from the velocity distribution assuming a succession of distinct types of ionization having the critical potentials 10.40, 10.63, 11.32, 11.80 volts respectively, and a probability law presented elsewhere in this paper. The portions *ACB*, *CED*, *DFG*, show the relative contribution of each type of ionization to the resultant ionization *ACEGH*. The agreement of *ACEGH* with the experimentally observed data *EI* is strong evidence in support of the assumed probability law and the assigned critical potentials.

Fig. 4. As in Fig. 3, the following critical potentials are estimated: 10.40, 10.63, 11.33, 11.71 volts, respectively.

were superposed on the polarization, indicating that errors of this origin were absent.

Finally, it was shown that the observed effects were independent of the small fields used to draw the positive ions out of the ionization chamber. This was demonstrated by taking data with potential differences between the grid and ionization chamber ranging from 0.02 to 3 volts.

Experimental Results

Figs. 3, 4, 5, and 6 represent typical results of the present experiments. The curves having black dotted points are the experimentally observed data while the curves drawn through circles are theoretically computed in a manner made clear in a subsequent paragraph.

For example let us consider Fig. 3. Curve *VD* is a plot of the velocity distribution of the electrons emerging from the final slit of the analyzing chamber and entering the ionization chamber, i.e., the ordinates are the observed electron currents into the ionization chamber corresponding to retarding potentials given by the abscissas. Thus, it is seen that the maximum energy of the electrons in this instance is in the neighborhood of 15 volts. The ordinates of curve *EI* represent the relative number of positive ions formed in the ionization chamber corresponding to retarding potentials given by the abscissas. Here it is seen that ionization is first noted when the retarding potential is reduced to approximately 4.6 volts. Thereby, the initial ionization potential is estimated to be 10.4 volts. We see that as the potential retarding the velocities of the ionizing electrons is decreased, the ionization increases gradually to 4.4 volts where it takes on a marked increase in the rate of increase. This change evidently marks another critical potential, that is, the setting in of another type of inelastic impact involving an energy transfer of 10.6 volts. For retarding potentials in the neighborhood of 4 volts the rate of increase of ionization with decrease in retarding potential falls off steadily to 3.7 volts where again the ionjzation rapidly increases. This

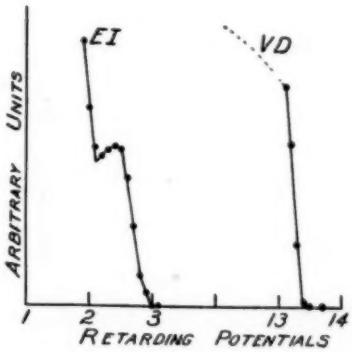

Fig. 5. The small velocity distribution brings out explicitly the decrease with increase in electron energy (over certain ranges) of the probability of inelastic impacts. The following critical potentials are estimated: 10.40, 10.60, 11.29 volts respectively.

step by step increase has been observed to progress for as many as six times, presumably constituting evidence of six distinct types of inelastic impacts of electrons with mercury atoms involving ionization. The curves of Figs. 4, 5 and 6 have a similar description and because of the different velocity distribution in each case they exhibit the information on the ionization of mercury vapor in various forms.

Inspection of these curves reveals at once that the original objective —precise determination of critical potentials—has been attained and further brings to light intensely interesting information of an unexpected sort; for it is seen that the probability of ionization in mercury vapor does not increase quite linearly from zero at the ionization potential

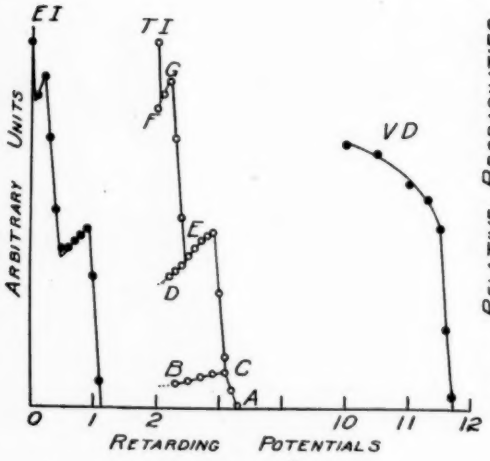

Fig. 6

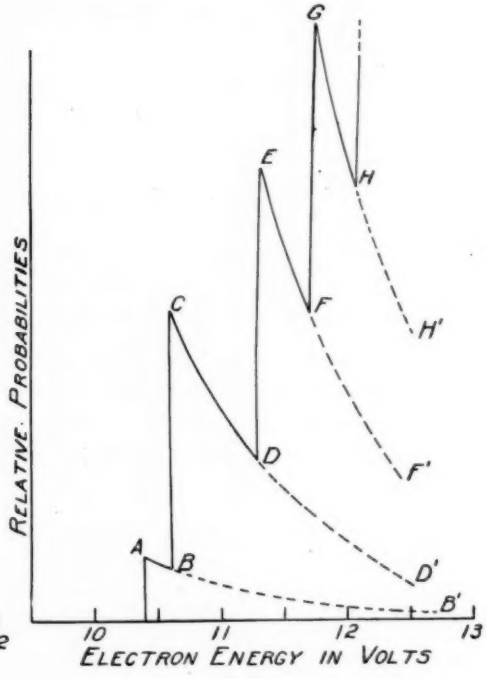

Fig. 7

Fig. 6. The theoretical curve *TI* is computed on the basis of the following critical potentials: 10.40, 10.59, 11.27, 11.63 volts. The absence of observed ionization corresponding to the initial two points of the curve *EI* is not clear but probably is due to momentary fluctuation in experimental conditions. The agreement of the experimental data with *TI* over the major portion of its extent is most striking. The critical potentials recorded are: 10.59, 11.27, 11.63 volts.

Fig. 7. The ordinates record the relative probabilities of ionization of mercury vapor by electrons of energies corresponding to the abscissas. The heavy line *ABCDEF*, etc., represents the resultant ionization probability function while *ABB'* is the probability of 10.40 volt ionization, and the ordinates between *CDD'* and *ABB'* represent the probability of ionization of the 10.60 volt type, etc.

as has been thought to be the case. On the other hand, the data indicate that the *probability of ionization is finite at the ionization potential and decreases with increase in electron energy* to a point where it takes on a sudden increment. There is a further decrease with a second subsequent increment, etc. Detailed investigation of the matter demonstrates that the probability function varies in a manner represented by the heavy continuous line of Fig. 7. We are thereby led to the interesting inference that *there are a succession of distinct types of inelastic impacts above the ionization potential in mercury vapor whose probability of production* $P(e)$ *varies in each case according to an exponential law, viz.,*

$$P(e) = P_{e_0} \epsilon^{-10(e-e_0)/e_0}$$

where e *is the energy of the impacting electron and* e_0 *is the associated critical potential.* Thus, the probability of stimulation of any type of atomic energy transition involving ionization by impacts of slow moving electrons is a maximum when the impacting electron has just enough energy to carry through the process, and the general increase of the probability of ionization from the ionization potential observed by various investigators[3] in the past is evidence merely of a succession of more complicated types of energy transfer than simply the removal of an optical electron from the normal orbit to infinity.

Using this probability law we may compute the forms of the experimental ionization curves from the observed velocity distribution data assuming suitable critical potentials for the various types of atomic transitions. In this way we choose values for the critical potentials which fit the experimental curves not only at the break points but throughout their extent. This permits an unusual accuracy in determination of the critical potentials. On this basis, the circles of the theoretical curves *TI* of the various figures have been computed. The complete agreement with the experimental curves demonstrates the validity of the probability law here suggested as well as the critical potentials assigned. Thus the following critical potentials have been determined:

	10.41	10.62	10.30	
	10.33	10.52	11.20	
	10.40	10.63	11.33	11.71
	10.38	10.58		
	10.40	10.63	11.32	11.80
Average	10.39	10.60	11.29	11.75

The above constitute the most recent determinations and, as indicated under "Errors", are believed to be free of appreciable systematic errors.

[3] Complete references in paper by Compton and Van Voorhis, Phys. Rev. 27, 724 (1926).

Earlier determinations, although not trustworthy as absolute values, are useful in establishing differences between the various critical potentials and are recorded as follows:

10.40	10.60	11.35	11.70	
10.50	10.67	11.30	11.76	
10.40	10.60	11.29		
	10.59	11.27	11.63	
10.43	10.58	11.22	11.62	
10.62	10.84	11.54		
		11.20	11.60	11.96

Of the first group perhaps the most accurate average value is the second critical potential—10.60 volts. Assuming this value the determinations recorded immediately above may be corrected leading to the following average values:

10.42 10.60(*assumed*) 11.28 11.67 12.03

A general consideration of the whole mass of experimental evidence leads to the following as the most probable values for the critical potentials:

10.40 10.60 11.29 11.70 12.06

The first three values are probably correct to 0.2 percent, the fourth has a probable error of 0.3 percent while the last is of uncertain precision. These probable errors have been assigned from detailed weighting of the experimental technique—a process less arbitrary and having more meaning than a straightforward computation of probable errors in the usual manner.

The region above twelve volts has been examined only very casually and evidence has been obtained of several higher critical potentials which are closer together. At the present time, however, no reliable information of these higher ranges may be given.

The data recorded in Fig. 6 typify results that have been obtained on occasions—especially in the earlier stages of the research—which are like the rest excepting that the first critical potential at 10.4 volts is conspicuously absent. It is seen that its apparent absence may be simply due to a fluctuation in experimental conditions such as to reduce the first one or two points of the ionization curve to the axis. Furthermore, the theoretically computed curve—on the assumption of existence of 10.4 volt ionization—is so well in accord with the experimental curve over the major portion of its length that it supports the conclusion that the 10.4 volt inelastic impact was truly present. In more recent determinations when presumably the most trustworthy results were obtained 10.4 volt ionization has always been present. The conclusion is, therefore, that there is only very meagre evidence of occasional absence of 10.4 volt atomic ionization.

The relative maximum probabilities of the several types of inelastic impacts are approximately as follows:

e_0	10.40	10.60	11.29	11.70
P_{e_0}	0.25	1.0	1.4	1.15

Theoretical Conclusions

A correspondence principle. Perhaps the most interesting result of this research is the fact that the probability of an inelastic impact of a particular type in mercury vapor has a maximum value when the impacting electron has just enough energy to carry through the atomic energy transition, the probability varying according to the law

$$P(e) = P_{e_0} \epsilon^{-10(e-e_0)/e_0}$$

It is remarkable that this law is of the same form as the probability function for the photoelectric ionization of caesium vapor as observed in some very beautiful experiments by Foote, Mohler and Chenault.[4] This correlation suggests the following generalization:

Light quanta and electrons obey the same general laws in processes involving ionization of atoms and molecules. In particular, the probability of atomic ionization of a certain type by a light quantum is the same function of its energy—excepting for constants—as the probability of the corresponding electron inelastic impact.

This generalization brings into accord a rather extended range of experimental facts. Foote, Mohler and Chenault found photo-electric ionization decreasing from the series limit according to the probability law here enunciated and also observed an unaccountably large probability of ionization well below the series limit (at λ2536A). In view of the present experiments and the correspondence principle here suggested, the large effect at λ2536A is interpreted to be direct evidence of a second type of ionization in caesium vapor—corresponding to the 10.6 volt ionization in mercury vapor. Moreover, the author's experiments[1] on photo-electric ionization of potassium vapor are consistent with the present hypothesis and the results obtained in caesium vapor as well as the experiments of Compton and Van Voorhis, Hughes and Klein and others on probabilities of ionization by electron impact. The photo-ionization of potassium vapor was produced by relatively wide bands of wave-lengths (about 100A) and therefore the detailed variation of the probability function was not observed. The general increase of the probability function from a threshold value through a maximum corresponds well to the observed impact ionization probability functions in various

[4] Mohler, Foote and Chenault, Phys. Rev. 27, 37–50 (1926).

vapors. The fact that the observed photo-electric threshold in potassium vapor was somewhat above the series limit is interpreted to be evidence that probabilities of the ultra-critical potential atomic transitions are so much greater as to mask the initial type of ionization.

The phenomena of the Compton effect[5] harmonizes with the suggested correspondence also. It has been known for a long time that ionization by electrons of great energy is in most cases a process that may be accounted for on the basis of classical laws, i.e., conservation of energy and momentum. Many experiments on ionization by beta rays and the absorption of beta rays in passing through matter support a theory worked out by Bohr[6] on this basis of classical electrodynamics. We would therefore infer from the general correspondence here suggested that for light quanta of great energy—high frequency—there is an ionization process which may be described by the classical laws of conservation of energy and momentum. *The Compton effect verifies this inference.*

Thus we must recognize a general similarity in ionization by light quanta and electrons. Of the many interesting speculative consequences of this correspondence mention should be made of the support of a new sort that it gives to the corpuscular light hypothesis. The analogy suggests that the interaction of radiation quanta and matter can be described by regarding the quanta as corpuscles of energy $h\nu$ momenta $h\nu/c$ and mass $h\nu/c^2$ traveling with the velocity of light c and exerting an inverse square electrical force field—traveling with infinite velocity—from an assigned virtual charge on the corpuscle.

The nature of the ultra-ionization potentials. The nature of the ultra-ionization energy transitions associated with the several observed critical potentials is as yet entirely speculative. Perhaps the most plausible view is that they involve ejection of one electron in the usual manner and simultaneous removal of another optical electron to a higher energy state (though the separations of the critical potentials are only fractions of a volt and are too small to correspond to spark spectra). A further suggestion is that these critical potentials are concerned with mercury molecules and perhaps are to be identified with energy levels associated with band spectra. Finally, it has been suggested* that the magnetic field—about 3 gauss—is concerned with the phenomena. It is possible that the atoms were oriented in several positions and each orientation possessed a distinct probability of excitation, etc. This view is supported by the fact that these critical potentials have not been observed in former

[5] A. H. Compton, Phys. Rev. 21, 483 (1923).
[6] N. Bohr, Phil. Mag. 30, 581 (1915).
* I am indebted to Dr. T. H. Johnson for pointing this out.

impact ionization experiments where presumably the magnetic fields present were considerably smaller (i.e., earth's field), though it seems at least the 11.3 critical potential should have evidenced itself.

The ratio e/h. The Bohr theory leads to an evaluation of the Rydberg constant in terms of known spectroscopic data and the two physical constants—the charge on the electron "*e*" and Planck's constant "*h*."[7] It is clear therefore that a measure of the ratio e/h (in conjunction with the Rydberg constant) enables a determination of both e and h. Assuming the smallest ionization potential V observed in these experiments to be associated with the series limit frequency ν according to the relation

$$Ve = 300h\nu$$

we have for the ratio e/h

$$e/h = 7.28 \times 10^{16}$$

which yields values of e and h in agreement with the accepted values[8] within the estimated experimental probable error of 0.2 percent.

I wish to thank Dr. W. E. Forsythe, Director of Nela Research Laboratory, for a supply of tungsten required in this research and I should like to acknowledge the skillful assistance of Mr. Enersen and Mr. Pechar, laboratory mechanicians. I am indebted to Professor Leigh Page, Professor A. H. Compton, Dr. F. L. Mohler, and Professor E. C. Kemble for discussions of phases of the work. Finally, it is an especial pleasure to record my indebtedness to Professor W. F. G. Swann who has maintained a stimulating and intimate interest in the research from its inception.

SLOANE LABORATORY,
YALE UNIVERSITY.
August, 2, 1926.

[7] Discussed in Sommerfeld's "Atomic Structure and Spectral Lines."
[8] See Millikan, The Electron; Birge, Phys. Rev. **14**, 361 (1919).

THE SIGNIFICANCE OF CERTAIN CRITICAL POTENTIALS OF MERCURY IN TERMS OF METASTABLE ATOMS AND RADIATION

By Helen A. Messenger

Abstract

The critical potentials of mercury, as found by Franck and Einsporn using the modified Lenard method, were studied by a further extension of this method which separated the effects due to metastable atoms and those due to true radiation. Quartz and calcite filters were interposed between the excitation system (hot-cathode and grid) and the detecting system ("photo-electric" plate and grid) of a four-electrode tube containing mercury vapor. The critical potential curves ("photo-electric" current plotted against voltage on excitation system) taken with and without these filters interposed were compared, the difference in the currents giving a measure of the relative number of metastable atoms produced at each voltage. All the breaks found by Franck and Einsporn except those at 5.76, 6.73, and 8.35 volts were found to be associated with increased production of metastable atoms. The hitherto unexplained breaks found by them at 6.04, 6.30, 7.12, 7.46, and 8.09 volts were found to be due mainly to the formation of metastable atoms. The difference between the photo-electric currents with the quartz and calcite filters interposed gave a measure of the radiation lying between λ1650 and λ2200, that is of the molecular bands λ2140 and of λ1849. The latter radiation was found to be the cause not only of the 6.7 volt break but also of that at 8.35 volts. The break at 7.73 volts is interpreted as the combined effect of radiation due to excitation at 7.69 volts and at 7.83 volts. The use of "photo-electric" plates of metals with different photo-electric characteristics gave further checks on the above conclusions.

THE critical potentials of mercury have been studied in great detail both by spectroscopic methods and by the Lenard method in various forms. As adapted by Davis and Goucher[1] in determining the nature of the resonance potentials at 4.9 and 6.7 volts and the ionizing potential at 10.4 volts, the Lenard method employs an excitation system having a hot cathode as a source of electrons surrounded by an accelerating grid to give them the desired velocities and a detecting system consisting of photo-electric plate and grid. By this method Franck and Einsporn[2] located eighteen critical voltages of which thirteen correspond to recognized energy levels at which either radiation occurs or the atom is known to become metastable, and five remain unexplained. Webb, using voltages not exceeding 5.2 volts and a photo-electric plate of nickel, found that in this case practically all the "photo-electric" effect was due

[1] Davis, B. and Goucher, F. S., Phys. Rev. 10, 101 (1917).
[2] Franck, J. and Einsporn, E., Zeits. f. Physik 2, 18 (1920).

to the action of metastable atoms on the plate.[3] He found further that with a quartz filter between the excitation and detecting systems the plate current for all voltages was greatly diminished and that below 6.0 volts no photo-electric current could be detected. The present experiments were undertaken to determine in greater detail the part played by metastable atoms at the various critical potentials and that by the radiant energy resulting from the excitation of the atom.

The essential feature of the method here used is to obtain "photo-electric," or better "plate" current-voltage curves by the method outlined above with and without filters of quartz or calcite interposed between excitation and detecting systems. These filters transmit certain radiations but cut off atomic carriers of energy, i.e., metastable atoms. By subtracting the plate current obtained with the quartz filter interposed (after correcting for its light absorption characteristics) from the plate current obtained without a filter a measure of the number of metastable atoms formed was obtained.

By using filters with known transmission characteristics and plates of different materials, the method was extended to identify some of the radiations excited at the various critical voltages and to show the relative importance of the effects due to these radiations and to metastable atoms.

Apparatus and Experimental Procedure

Three four-electrode tubes designated as tubes I, II and III were used. In Fig. 1 the essential details of tubes II and III are given. The uni-potential hot-cathode F was of the form described by Webb.[3] The glass tube supporting it was held in a ground glass joint and extended perpendicular to the plane of the diagram. The cylinder G is the accelerating grid surrounding the hot-cathode F. The "photo-electric" plate P was supported by an insulating quartz tube through which the lead wire passed to the electrometer connection at E. The slide S carrying three windows, one open, the other two covered respectively with quartz and calcite, moved easily in the nickel frame D, which, for rigidity, was of sheet metal with the exception of the side facing the cathode, where nickel mesh was used. An opening in this frame D opposite the plate P and in line with the hot-cathode F was covered by the "photo-electric" grid H. By turning the winch W in its ground glass joint the quartz or calcite filter could be lowered so as to cover this opening. As the semi-cylindrical nickel box B which surrounded the plate P was light-tight and welded to D the only entrance to the plate P for radiation or metastable atoms was through H.

[3] Webb, H. W., Phys. Rev. **24**, 113 (1924).

Tubes II and III were identical except that in tube II the plate was of nickel and in tube III of aluminum. With the exception of this aluminum plate and of the platinum cathode all metal parts in all three tubes were of nickel.

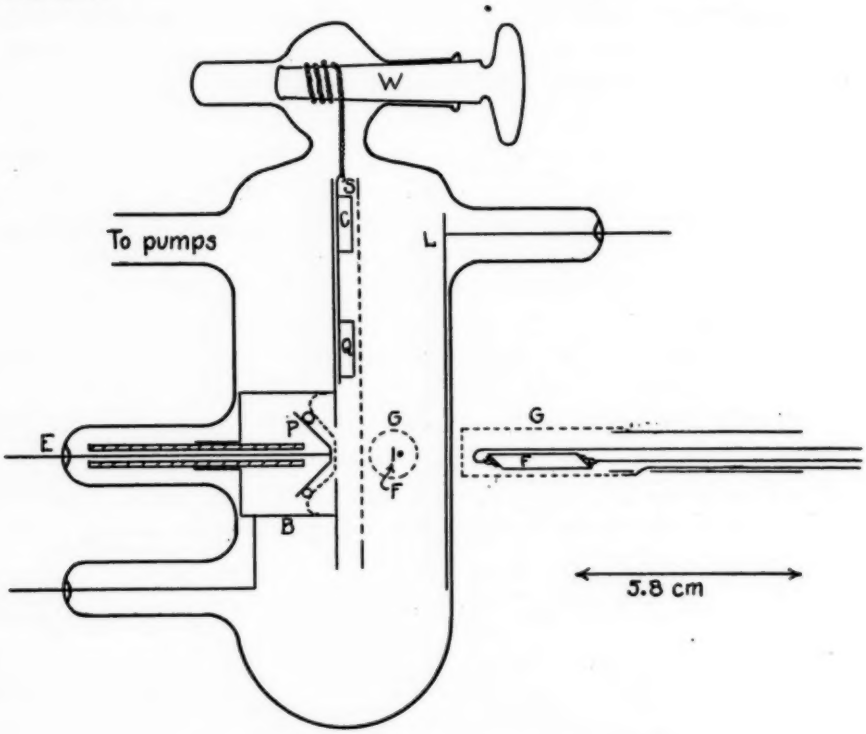

Fig. 1. Diagram of experimental tubes II and III.

The plate *P* was a disk folded along a diameter so that the halves formed an angle of about 90° (the fold being placed parallel to the cathode). The grid *H* was bent to the same general form and insulated from the plate by small quartz rods. This form of the detecting system was used to avoid possible effects due to the collecting of electrons on the face of the quartz toward the plate which would tend to inhibit further photo-electric action.

Tube I differed from the above in that it lacked the sliding windows and had a plate of different form. Filters of quartz and calcite were placed inside the tube when it was blown. A side tube of which the end could be opened made it possible to reach in with forceps and place in position either the quartz or calcite filter, after which the tube was resealed. The advantage of this arrangement was that larger windows

and filters could be used which increased the plate current making it possible to locate the critical points on the curves with greater precision. This tube was used to study the details of the individual curves. The plate was a disk mounted with its surface parallel to the plane "photoelectric" grid at a distance of 3 mm. When in use the quartz window rested against this grid so as completely to cover the opening to the box containing the plate and to prevent the entrance of the metastable atoms.

In all these tubes a metal lining L which was kept at a known voltage prevented the collecting of charges on the glass wall which might result in spurious breaks in the curves,[4] and also served to shield the tube from outside disturbances. The tube was further shielded by metal foil wrapped closely about the outside and well grounded.

The temperature of the walls of the tube was held constant to within 0.5°C by a low speed fan which forced air heated by coils of wire in an adjoining oven into the asbestos lined box containing the experimental tube. The air flow was controlled by baffle plates adjusted until they kept the temperature uniform throughout the box.

The tube was pumped until the pressure of the residual gas was less than .0002 mm by means of a Langmuir condensation pump in series with a fore-pump. The pumps were kept running during readings.

Plate currents were measured by a Compton electrometer with a sensitivity of 2000 mm per volt. Accelerating voltages were measured by a Wolff potentiometer. The emission current was measured by a microammeter in the cathode-grid circuit The microammeter reading was taken simultaneously with each electrometer reading. The current E plotted on the curves in this paper is the electrometer current divided by the emission current.

Throughout the experimental work the negative end of the platinum strip which formed the heater of the cathode was in electrical contact with the surrounding equipotential sheath which was insulated from the heater at all other points The accelerating voltage was applied between this equipotential point and the grid G. The measured accelerating voltage was therefore the maximum voltage drop that could be obtained between the grid G and any part of the hot-cathode.

The voltage correction for drop in the leads and contact potential difference was obtained by locating the ionization point by the method of Davis and Goucher[1] and checked by the value of the lowest critical potential, 4.7 volts, which was always found as a well defined break in the resonance potential curves when no filter was interposed between

[4] Olson, A. R. and Young, T. F., Phys. Rev. **25**, 58 (1925).

the excitation and detecting systems. When the curves were corrected certain marked peculiarities of form which characterized the various curves were repeated at the same voltages and gave additional evidence of the accuracy of the correction. Throughout this paper the correction has been applied to all voltages cited and plotted on curves.

As the "photo-electric" sensitivity of the plate P varied with time, it was necessary, for a reliable comparison of the effects on the plate when no filter was used and when a quartz or calcite filter was interposed between the excitation and detecting systems, to obtain data for the resonance potential curves rapidly. With the sliding windows of tubes II and III it was possible to remove either filter and leave the window open or to close the window by interposing either filter in approximately one second. As a result the total time required to measure the plate current for all three windows at a given voltage was reduced to that required for the readings alone. To avoid the effect of changes in the plate on the form of the curve as a whole these sets of three readings were taken at .5 volt steps and the details interpolated from curves taken separately at consecutive .1 volt steps from 4.0 to 11.0 volts for each filter and for no filter but at the same temperature and with the same distributions of voltage.

The filters of quartz and calcite and the plate materials nickel and aluminum were chosen because they separated the effects of the various radiations emitted to the best advantage. The properties which led to their selection are summarized below to aid in the interpretation of the curves which follow. The wave-length ranges of the radiations in mercury vapor which can and can not be detected by the present apparatus are also specified.

Properties of filters and plates

Filter	Minimum wave-length transmitted	More than 60 percent transmitted	Important mercury lines and bands not transmitted
Quartz	1650A[5]	$\lambda > 1800$A[5]	1403, 1269A
Calcite	2200A[5]	$\lambda > 2400$A[5]	2140, 1849A 1403, 1269A

Plate	Photo-electric long wave-length limit	Photo-electric effect of $\lambda 2537$
Nickel	2500A[6]	Not measurable
Aluminum	2700A[6]	Marked

WAVE-LENGTH RANGES OF THE RADIATION DETECTED BY THE PRESENT APPARATUS

Less than 1650A.—These wave-lengths affect the plate when no filter is used but their effect is not separable from that of metastable atoms. Owing to the large effect of the latter the effect of these short waves is considered negligible.

1650–2200A.—This wave-length range is transmitted by quartz but not by calcite. The response of the plate to it is given by the difference between the photo-electric currents when using quartz and when using calcite as filter.

[5] Pflüger, Phys. Zeits. 5, 215 (1904).

2200–2500A.—This range of wave-lengths is transmitted by calcite and produces a photo-electric current from the nickel plate.

2200–2700A.—This range of wave-lengths is transmitted by calcite and produces a photo-electric current from the aluminum plate.

2500–2700A.—This range of wave-lengths is transmitted by either filter and produces a photo-electric current from aluminum but not from nickel.

WAVE-LENGTH RANGE OF RADIATION WHICH PRESENT APPARATUS CANNOT DETECT

Greater than 2700A.—These which are not detected by either plate are in the visible and infra-red regions of the spectrum and form a large part of the total radiation.

The transmissibilities of the filters were tested before they were used and after they had been in the tube for several months. They were found to be unchanged provided they had not been exposed to the arc used to sensitize the hot-cathode.

The photo-electric threshold of nickel has been given by Nielsen[6] as approximately 2500A. As he worked with outgassed metal while the plates used in the present experiment were only cleaned and sand-papered this upper wave-length limit was verified for the nickel plate used, by focussing on the plate monochromatic light from a metal spark dispersed by a quartz spectrograph. The effect of 2500A was not measurable while that of 2300A was marked. Evidently the nickel plate used did not respond to λ2537 to a measurable extent.

RESULTS AND DISCUSSION

The results of the measurements are given by curves in Figs. 2, 3, 4 and 5, and in Table I.

Fig. 2 shows three typical curves obtained with tube II (nickel plate). Curve (*a*) is that taken with no filter; curve (*b*) is that with the quartz filter in place; curve (*c*) with the calcite filter in place. Curve (*a*) shows all the critical points found by Franck and Einsporn. (See Table I, column 1.) The most notable feature of this set of curves is the large decrease in the plate current when either filter is interposed. The ratio of the plate current measured when using no filter to that when using a quartz filter is at times as high as 30:1 for voltages above 6 volts; its value is least between 5.3 and 6.0 volts; below 5.3, the lowest voltage at which radiation is detected, (see curves (*b*) and (*c*)) the value of this ratio approaches infinity.

It may be observed that although curve (*a*) (no filter) shows the same critical points as (*b*) (quartz filter) above 5.3 volts, the curves are not similar in form, as (*a*) builds up more rapidly at low than at high voltages and (*b*) builds up more rapidly at high than at low voltages. The calcite curve (*c*) shows no critical points at 5.7, 6.7, and 8.3 volts, and the break

[6] Nielsen, J. R., Phys. Rev. 25, 30 (1925).

TABLE I

Critical potentials of mercury and some interpretations of their significance

Given by Franck and Einsporn.	Calculated from theory[9]	Interpreted from theory[9]	Found experimentally using—				As interpreted from curves and data here given.	
			no filter	quartz filter	calcite filter	Plate	Type of radiation indicate or implied	Number of metastable atoms.
1	2	3	4	5	6	7	8	9
4.68	4.66	$1S-2p_3$	4.70	....	....	Ni	None	Medium
			4.70	....	....	Al		
4.9	4.86	$1S-2p_2$	4.90	....	....	Ni		Small
			4.90	4.90	4.90	Al	2537, $1S-2p_2$	
5.3	5.28–5.34	Molecular band 2338–2313	5.25	5.25	5.25	Ni and Al	$\lambda<2500, >2200$ probably 2338–2313	Medium (molecules)
5.47	5.43	$1S-2p_1$	5.45	5.40	5.40	"	2537, $1S-2p_1$	Large
5.76	5.73	Ionization						
	5.77	Molecular band 2140	5.75	5.75	....	"	$\lambda<2200, >1650$ probably 2140	None
6.04	....		6.00	6.00	6.00	"	$\lambda>2200, <2700$	Large
6.30	....		6.30	6.30	6.30	"	$\lambda>2200, <2700$	Small
6.73	6.67	$1S-2P$	6.70	6.70	....	"	1849, $1S-2P$	None
7.12	....		7.10	7.10	7.05*	"	$\lambda<2200, >1650$	Medium
7.46	....		7.45	7.45	7.45*	"	$\lambda<2200, >1650$	Large
	7.69	$1S-2s$				"	4046, $2p_3-2s$ 4358, $2p_2-2s$ 5461, $2p_1-2s$	Medium
7.73			7.75			"	2537, $1S-2p_2$	
	(7.83)	$(1S-2S)$		7.80	7.80*	"	4077, $2p_2-2S$ 10139, $2P-2S$ 1849, $1S-2P$	
8.09	....		8.00	8.05	....	"	$\lambda<2200, >1650$	Very small
8.35	....		8.30	8.30	....	"	$\lambda<2200, >1650$ probably 1849	None
8.64	8.58	$1S-3p_{2,3}$	8.60	8.60	8.60	"	13672, $2s-3p_2$ 13950, $2s-3p_3$ 4046, $2p_3-2s$ 5461, $2p_1-2s$	Very small
8.86	8.79	$1S-3P$	8.80	8.85	8.80*	"	$\lambda<2200, >1650$	
	8.80–8.82	$1S-3D$ $1S-3d_{1,2,3}$					5791, $2P-3D$ 1849, $1S-2P$	
	8.80	$1S-3p_1$					3663, $2p_1-3D$ 3131, $2p_2-3D$ 2967, $2p_3-3D$	Small
....	9.15	$1S-3s$	9.15	9.15	9.20	"	3341, $2p_1-3S$	Very small
	9.19	$1S-3S$					2894, $2p_2-3S$ 2735, $2p_3-3S$	
9.37	9.32	Successive impacts $1S-2p_2$	9.30	9.30	....	"	None	Large
9.60	9.52	Successive impacts $1S-2p_2$ $1S-2p_3$	9.50	9.55	....	"	2537, $1S-2p_2$	Medium
9.79	9.72	Successive impacts $1S-2p_2$	9.70	9.70	9.70	"	2537, $1S-2p_2$	Small
10.38	10.39	Ionization	10.4	10.4	10.4	"	All types	Medium

* Weak break.

Precision of observed critical points ±• .05 volt.

at 8.1 volts is missing or very weak. In general the breaks above 8.0 volts on all curves taken with the calcite filter in place are difficult to locate precisely as none of them are well defined.

Measurements were made at 28°C, 55°C and 89°C. Those given in the form of curves in Fig. 2, taken at 89°C, are typical of all those obtained.

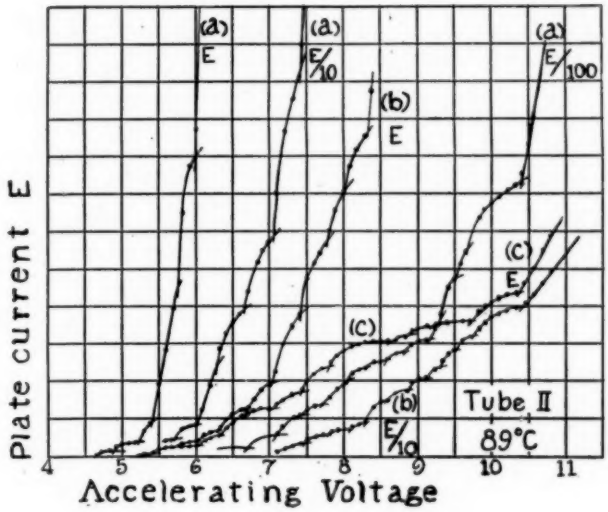

Fig. 2. Curves obtained with tube II (nickel plate), (*a*) using no filter, given in three parts with the electrometer current for two parts reduced by 10 and 100 for convenience in plotting, (*b*) using the quartz filter, given in two parts, (*c*) using the calcite filter.

At the higher temperatures the plate currents were larger at all voltages on all three curves; the ratio of the plate current with no filter to that due to radiation transmitted by quartz showed no significant change.

Fig. 3 shows how the metastable atoms increase with accelerating voltage. The ordinates are the differences between plate currents obtained at the stated voltages with and without the quartz filter between the excitation and detecting systems. They are therefore the differences between the plate current due to all forms of energy reaching the plate and that due to energy which reaches it as radiation. This curve is in three parts, the ordinates being reduced as indicated. The fact that this curve rises markedly at 4.7, 5.4, 7.8 and 8.8 volts indicates a marked increase in metastable atoms as a result of excitation at each of these voltages. It is known that metastable atoms are formed at levels corresponding to the two lower voltages, 4.7 and 5.4 volts (see Table I, column 3). Corresponding to the two higher voltages, 7.8 and 8.8, theory

predicts that there are energy levels from which the valence electron may drop to either one of these metastable $2p$ orbits by emitting radiations which give rise to known spectrum lines (see Table I, columns 8

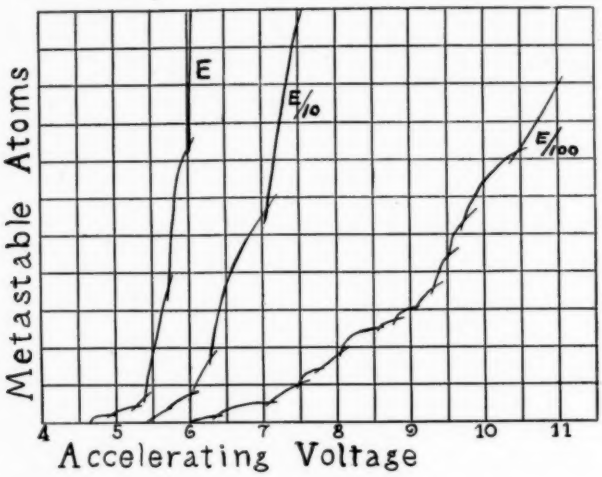

Fig. 3. Increase of metastable atoms with voltage. The ordinates are the differences between those of curve (*a*) and curve (*b*) in Fig. 2 at the voltages indicated.

and 9). The heretofore unexplained breaks of Franck and Einsporn at 6.0, 6.3, 7.1, 7.45 and 8.1 volts also occur on this curve. (The break at 8.1 volts is not listed by Franck and Einsporn but appears on their published curves.[2]) This indicates either that there are metastable levels corresponding to these critical voltages or else that the excitation at these voltages results in electron transitions to metastable orbits with or without radiation.

Fig. 4 shows the difference between photo-electric currents when quartz and calcite filters were used, plotted against accelerating voltage. This curve rises sharply at 6.7, 7.45 and 8.3 volts and to a lesser degree at 7.8 and 8.8 volts indicating that at these voltages there is an increase of radiation of wave-length less than 2200A but greater than 1650A since this is the range of the wave-length transmitted by quartz but not by calcite. The fact that this curve begins at 5.75 volts is of especial interest. The radiation from 5.75 to 6.7 volts is probably that of wave-length 2140A due to the molecular band at 5.73 volts observed by Wood and Guthrie,[7] as is suggested by Mohler.[8] At and above 6.7 volts the radiation represented by this curve is probably mainly $\lambda 1849$.

[7] Wood, R. W. and Guthrie, D. V., Astrophys. J. **29**, 211 (1909).

[8] Mohler, F. L., National Research Council Bulletin, No. 48, Part II, pp. 70–71 (1924).

Fig. 5 shows three curves obtained (*a*) with no filter, (*b*) using the quartz filter, and (*c*) using the calcite filter with tube III (aluminum plate). Any differences between these curves and those of Fig. 2 must be due solely to the differences in the properties of the plates. Above 7.5 volts the two sets are similar in form; consequently only the parts of the curves for lower voltages are reproduced here. In curve (*a*) where no filter was used the lowest critical point is at 4.70 volts; in curves (*b*) and (*c*) the pure radiation curves, at 4.90 volts. This confirms the conclusion that the plate current from 4.70 to 4.90 volts is due solely to

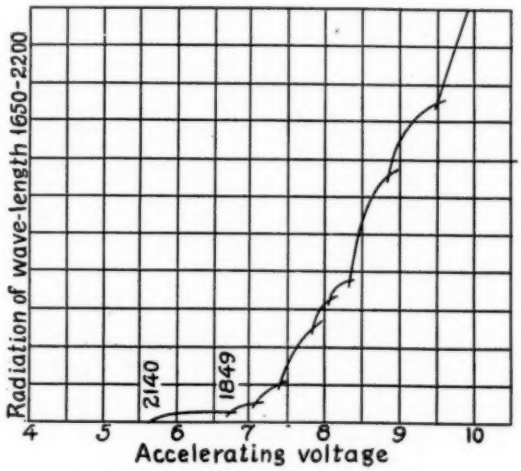

Fig. 4. Radiation of wave-length between 1650 and 2200. The ordinates are the differences between those of curves (*b*) and (*c*) in Fig. 2.

metastable atoms and is not a true photo-electric current. The radiation which is responsible for the initial rise in (*b*) and (*c*) is λ2537, which affects the aluminum plate. It may be observed that the ratio of the total plate current represented by (*a*) to the current due to pure radiation represented by curve (*b*) is smaller for the curves in Fig. 5 than for those in Fig. 2 due to the increase in the photo-electric current at all voltages resulting from the action of λ2537.

The breaks at 4.9 and 9.7 volts were attributed in the curves of Franck and Einsporn to λ2537, two successive impacts taking place at the higher voltage. The fact that the photo-electric response of the nickel plate used in the present experiment to that radiation is so small compared with its response to energy carried by metastable atoms makes it unlikely that this is the explanation of the breaks at these voltages in Fig. 2. They are probably due to a small number of metastable atoms produced as the

valence electron drops from the 4.9 to the 4.7 orbit as the result of an atomic impact.

As stated earlier in this paper the value of the emission current was read simultaneously with each value of the plate current. When readings were taken with increasing accelerating voltage the emission current also increased and, plotted against this voltage, gave a curve in which there were upward breaks coinciding in many cases with the critical potentials. When the voltage was varied in the reverse direction the tendency of the emission curve to drop at these potentials was less marked. It was found that dividing the electrometer current by the emission current in no case removed from the resonance potential curves

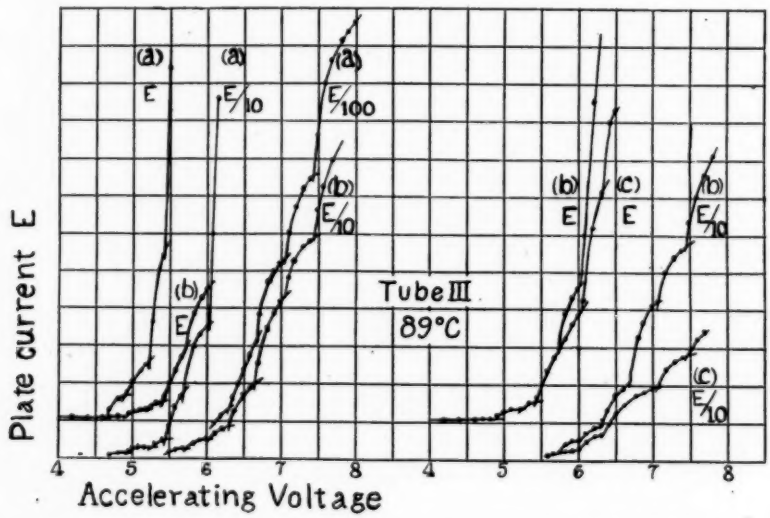

Fig. 5. Curves obtained with tube III (aluminum plate), (*a*) using no filter given in three parts the electrometer current for two being reduced by 10 and 100 for convenience in plotting, (*b*) using the quartz and (*c*) using the calcite filter, each given in two parts. Curve (*b*) is given twice, on the left with (*a*), on the right with (*c*) for clearness.

the breaks at the critical points recorded in the results (see Table I), whereas other intermediate spurious breaks observed on curves in which the electrometer reading was plotted directly, were eliminated.

Table I gives a summary of the experimental results. Column 1 gives for comparison the critical potentials found by Franck and Einsporn[2]; column 2 the corresponding values as calculated from theoretical considerations; column 3 gives the interpretation from the Bohr theory of the Franck and Einsporn critical points as given by Mohler[8]; columns 4, 5 and 6 give the critical points obtained in the present work with the

filters listed at the heads of the columns; the plates used are specified in column 7.

Columns 8 and 9 give the author's interpretations of the experimental results, column 8 giving a description of the types of radiation indicated and column 9 indicating the relative number of metastable atoms produced at the various critical voltages. The manner in which these interpretations were reached has been discussed in the cases of some of the critical points, e.g., 4.7, 4.9, 5.4, 5.75 volts, etc.; the interpretations for other points are self-evident, e.g., those for 9.3, 5.25 and 6.7 volts; a few more need explanation.

It has been shown in connection with Fig. 3 that as a result of the excitation at the heretofore unexplained critical voltages 6.00, 6.30, 7.10, 7.45 and 8.10 volts metastable atoms are formed. The excitation at certain of these voltages also results in radiation of which the wave-length has been identified in some cases. At 6.00 and 6.30 volts, however, the evidence is not conclusive. At these voltages on both radiation curves obtained with the nickel plate the breaks are of similar magnitude. This indicates radiation of wave-length between 2200 and 2500A. On both curves with the aluminum plate these breaks are again similar to each other in magnitude but of greater magnitude than with the nickel plate. This indicates radiation of wave-length between 2200 and 2700A, which may be greater or less than 2500A. The increased magnitude of the 6.00 and 6.30 volt breaks with the aluminum plate may therefore be due either to λ2537 or to the band λ2338–13, the shorter wave-length radiation being more effective on the aluminum plate than on the nickel plate since it is farther from the upper photo-electric limit.

At 7.05, 7.45 and 8.05 volts, the fact that the breaks are weak or missing on the calcite curves, indicates the presence at these levels of radiation of wave-length $<$2200A and $>$1650A—probably λ2140 or λ1849.

The interpretation of breaks at higher levels is complicated by the fact that these levels are increasingly close and the radiation increasingly complex. It is not possible to do more from the present data than indicate a few facts that seem evident.

The break at 7.75 volts on the no-filter curves obtained with either nickel or aluminum plate is of interest as showing the possibilities of this method. The computed value corresponding to the $2s$ level is 7.69 volts; that corresponding to the $2S$ level is 7.83 volts. Mohler notes that the electron transition to the $2S$ level is not indicated in the Franck and Einsporn curves.[8] (It is given in brackets for that reason in columns 2 and 3 in Table I.) On the radiation curves in the present experiment the

break always came at a higher voltage (7.83 volts) than on the curves taken with no filter (7.75 volts). It is evident that the 7.75 volt break is an average of the 7.69 volt break, due mainly to metastable atoms (see Fig. 3) and the 7.83 volt break due mainly to radiation. The observed effect of radiation is small at 7.69 volts because the electron transitions from the $2s$ to the metastable $2p$ orbits and to the $2p_2$ orbits give rise to visible radiations which cannot affect the plates and the effect of $1S-2p_2$ is weak in comparison with the effect of metastable atoms; it is larger at 7.83 volts since from the $2S$ level the transition $2P-2S$ may be followed by $1S-2P$, λ1849. That this is the correct explanation of this break is proven by the rise in the curve of Fig. 4 and the weak break in the calcite curve at 7.80 volts.

In all curves from measurements made with all three tubes when using the quartz filter, a well-defined break occurs at 8.30 volts, marking the excitation of a radiation that affects the slope of the entire curve above that point. There is no corresponding break on the calcite curve, so that beyond this voltage the two radiation curves are markedly unlike in form. This means that at 8.30 volts there is a large increase of a radiation of wave-length >1650A and <2200A which probably is λ1849, $1S-2P$. The next lower level corresponding to a known voltage is the $2S$ level corresponding to 7.83 volts. The known radiation λ10139 excited at 7.83 volts accompanies the electron transition $2P-2S$. If the excitation at 8.30 volts results in an infrared radiation as the valence electron moves to the $2S$ orbit it may be followed by the radiation $2P-2S$, λ10139, and then by $1S-2P$, λ1849. The two infrared radiations are beyond the wave-lengths detected by this apparatus but there is evidence of the existence of λ1849. Further evidence in favor of this interpretation of the 8.30 break is given by Eldridge[9] who reported that at 8.4 volts $2P-2S$, λ10139 was the strongest line in the observed spectrum although it did not appear on his published plates, as it fell in the infrared.

The break at 8.65 volts indicates electron transitions from the $3p_{2,3}$ levels accompanied by radiation of wave-length not detectable with this apparatus which finally leaves the valence electron in a metastable orbit. Since the infrared radiations λ13672 and λ13950, $2s-3p_2$ and $2s-3p_3$ are recognized radiations, it is probable that these occur and are followed by $2p_3-2s$ and $2p_1-2s$, in the visible region. This would account adequately for the small number of metastable atoms observed at 8.65 volts.

The question as to whether the large current attributed to metastable atoms might not be due in part to ionized atoms, was carefully in-

[9] Eldridge, J. R., Phys. Rev. 23, 685 (1924).

vestigated by the method of Davis and Goucher.[1] Making the photo-electric grid negative with respect to the plate but keeping all other voltage distributions unchanged radiations and metastable atoms will produce a negative "photo-electric" current, while ionized atoms will tend to charge the plate positively and therefore decrease the negative current. With the grid positive with respect to the plate, radiation, metastable atoms and ionized atoms will produce a positive current. Consequently, if in comparing the plate currents obtained with these two arrangements of voltage the ratio of the positive to the negative is constant for all voltages, either the number of ionized atoms being formed is always proportional to the plate current (which is not probable) or the number formed is negligible. An increase with voltage in the ratio of the positive to the negative current would indicate the formation of ionized atoms at those voltages at which the ratio increased. No evidence of ionization was found below 10.4 volts. Furthermore a very careful study of that part of the curve between 5.0 and 6.0 volts showed that ionization was not the cause of the 5.7 volt break on the curves obtained with this apparatus.

It is of interest to compare the results of Franck and Einsporn with those given here. Evidently the effect of radiation was relatively greater in their apparatus, that of metastable atoms less. In the present apparatus the effect of radiation was the smaller of the two. The reason for these differences in sensitivity of the apparatus is not clear. With the exception of 4.70 volts, the voltages at which they report strong breaks are those at which the present work indicates the production of radiation. The breaks which are marked in the metastable atom curve of Fig. 3 are all listed among their weak breaks. The exception is the break at 8.35 volts which they list as a weak break although its interpretation in this work indicates that it is due to radiation.

The writer takes pleasure in acknowledging her indebtedness to Professor Harold W. Webb who suggested both the problem and the general method of attacking it and who has contributed much valuable criticism throughout the course of the work.

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June 26, 1926.

THE LACK OF EFFECT OF A MAGNETIC FIELD ON THE DIELECTRIC CONSTANT OF HCl AND NO

By Lewis M. Mott-Smith and Charles R. Daily

Abstract

Using an electron tube method, experiments have been performed to test whether the dielectric constant of HCl and NO gases changes when a strong magnetic field is applied. The magnetic field strength was 4800 gauss and the apparatus was capable of definitely detecting a change in dielectric constant of one part in 100,000. The gases were tested at pressures of from about 2 to 40 cm of mercury, at room temperature, and with the magnetic field both parallel and perpendicular to the electric field. No change was detected under any conditions.

RECENT theoretical investigations by Debye,[1] Ruark and Breit, and others have made it of interest to look for a change in the dielectric constant of a gas when a strong magnetic field is applied to it. Experiments in search of this effect have been performed by Weatherby and Wolf.[2] They worked with helium, oxygen, and air and found that the dielectric constant of these gases does not change by more than one part in half a million when the gas is put into a magnetic field of 10,000 gauss. The dielectric constant was measured both parallel and perpendicular to the direction of the magnetic field with gas pressures of 20 cm for helium and 76 cm for air and oxygen. It is to be noted that none of these gases, helium, oxygen, or nitrogen, are gases of the so-called "polar" class, which means that their molecules are known to have only a very small permanent electric polarization. At the suggestion of Dr. Linus Pauling it was accordingly thought interesting to try gases having a strong permanent electric dipole. From the work of Zahn[4] HCl is definitely known to be such a gas. The strength of the electric moment of the NO molecule has not been directly measured but there is evidence that it also has a rather large electric dipole. It is of interest to try both gases since HCl is diamagnetic and NO paramagnetic.

The experimental procedure consisted in placing the gas to be investigated in a special parallel plate condenser which was placed between the pole pieces of a powerful electromagnet, and in noting whether the capacity of the condenser changed when the field was applied. To detect

[1] P. Debye, Phys. Zeits. 27, 67 (1926).
[2] A. E. Ruark and G. Breit, Phil. Mag. 49, 504 (1925).
[3] B. B. Weatherby and A. Wolf, Phys. Rev. 27, 769 (1926).
[4] C. T. Zahn, Phys. Rev. 24, 400 (1924).

a change in capacity a method was used similar to that first employed by Herweg and subsequently by several other investigators, including Weatherby and Wolf. In essence it consists in measuring the change in capacity by measuring the frequency produced in an oscillatory circuit formed by the condenser and an inductance. Continuous oscillations were maintained in this circuit by a special electron-tube oscillator circuit. To detect the change in frequency the main oscillator and another similar oscillator induced small e.m.f.'s in a detecting circuit, the difference in frequency being such that electrical beats were produced in this circuit. After rectification these became a low frequency alternating current which was then amplified and made to operate a simple oscillograph. The mirror of the oscillograph reflected light from a pinhole into a telescope and oscillated the spot up and down; the same beam of light was also reflected from a mirror attached to one of the prongs of an electrically driven tuning fork which caused the spot to oscillate horizontally. Lissajou's figures are thus produced when the two frequencies are commensurable. When they are not exactly commensurable but nearly so, the figure slowly changes from one shape to another. This arrangement gave us a sensitive method of detecting a change in the frequency of the beat note and consequently of detecting a change in the frequency of the gas-condenser-oscillator.

The gas-condenser was built up of interleaved flat copper plates, spaced about 1 mm apart and supported on a Pyrex frame. All the exposed metal parts were gold plated to prevent corrosion, the condenser was enclosed in a glass tube and attached to the gas generating and pumping apparatus. Its capacity when evacuated was measured by comparison with a standard and found to be 324×10^{-6} microfarad. The part of the capacity not influenced by the introduction of the gas was estimated to be only a few percent of the total capacity and it was therefore neglected in these experiments. To measure changes in capacity and to adjust the frequency of the oscillator to a stationary Lissajou figure a small variable condenser was connected in parallel with the gas-condenser. This was of the sliding coaxial cylinder type and was provided with a micrometer screw adjustment, the smallest division of which corresponded to a calculated change in capacity of 9.10×10^{-9} microfarad. The electron-tube driving circuit was designed so as to have as small an influence as possible on the frequency of oscillation, in order that accidental changes in frequency due to variations in battery e.m.f.'s, or other changes in the driving circuit, might be as small as possible. This circuit arrangement maintained very feeble oscillations in the condenser circuit so that the maximum electric field in the condenser was about ten volts per cm.

The frequency of oscillation was 168,000 cycles per second. The magnetic field was produced by a large electromagnet having flat pole faces to make the field as uniform as possible over the condenser area. The field strength was measured with a bismuth spiral and found to be 4800 gauss, and fairly uniform.

Preliminary experiments were made to see if any effect was produced by turning on the field while the condenser was evacuated, and to determine the sensitivity of the apparatus. It was found that at the instant of making or breaking the electromagnet circuit there was a slight jump in the figure but that after a few moments it again became stationary. To determine the sensitivity of our apparatus we first obtained a stationary figure, then changed the capacity of the variable condenser until the figure could definitely be seen to be changing. It was found that a change in capacity corresponding to 1/3 division produced an easily detected movement in the figure. Since 1/3 division corresponds to a change in capacity of 3.0×10^{-9} microfarads and the capacity of the gas condenser is 324×10^{-6} microfarads it is seen that our apparatus is capable of detecting a change in capacity of this condenser of about 1 part in 100,000.

The HCl gas was handled in a manner similar to that used by Zahn. It was generated by dropping concentrated H_2SO_4 on fused NaCl, passed over P_2O_5 and collected by condensation into a liquid air trap. When sufficient gas had been collected the generator was closed off, the trap and condenser pumped out over the frozen HCl and a portion of the gas allowed to evaporate into the condenser. The pressures used were about 2.5, 10, 19 and 42 cm of mercury. The magnetic field was applied both parallel and perpendicular to the electric field at each pressure. When the switch in the electromagnet circuit was closed no movement of the figure was detected at any pressure or direction of field, except the momentary jump mentioned above. This shows that to one part in 100,000 there is no change in the value of ϵ for HCl. Since the value of ϵ at room temperature and say 20 cm pressure is 1.0010 we would have been able to observe a change in $\epsilon-1$ of 1.0 percent.

The nitric oxide gas was generated by dropping H_2SO_4 into a solution of $NaNO_2$. It was passed through water to remove NO_2 and through H_2SO_4 to remove water vapor. Condensation by liquid air was found troublesome, hence the gas was collected into an evacuated chamber and thence allowed to escape into the gas-condenser. The pressures in this case were about 4, 13 and 40 cm and again tests were made with the field in both positions. No effect was detected. In order to be able to say what fractional change in $\epsilon-1$ would have been detected it was necessary to make a determination of ϵ since this quantity has not yet

been measured. A rough determination was made which gave at room temperature, and reduced to 76 cm pressure, the value 1.00044. The detectable percent change in $\epsilon-1$ can now be calculated and gives the value 8.3 percent for a pressure of 20 cm. It is interesting to note that the dielectric constant is about the same as that of air which makes it appear possible that the electric moment of the NO molecule is not as large as has been supposed.

Our work thus shows that there is no large change in the dielectric constant due to a magnetic field even for polar molecules. Other polar molecules could be tried but the interest is not great since we cannot expect any difference in behavior. These experiments together with those of Weatherby and Wolf, therefore complete the experimental side of this question until a method more sensitive than one part in 100,000 is devised.[5] Experiments in this direction are now in progress.

NORMAN BRIDGE LABORATORY,
June 18, 1926.

[5] The authors feel that the sensitivity claimed by Weatherby and Wolf is a little too high. By using the method which Weatherby and Wolf used of counting beats for a few seconds before and after the field is applied we also obtained results for which we could claim as high sensitivity. It is believed that the sensitivity determined in the manner explained above is the true one for our apparatus and that Weatherby and Wolf's results are reliable to no greater accuracy.

ON THE QUANTUM THEORY OF THE SPECIFIC HEAT OF HYDROGEN

PART I. RELATION TO THE NEW MECHANICS, BAND SPECTRA, AND CHEMICAL CONSTANTS

By J. H. Van Vleck

Abstract

1. If in the new quantum mechanics the hydrogen molecule is treated as a simple rotating dipole like HCl, the a priori probability is $2m$, and the rotational quantum number assumes the values $m = \frac{1}{2}, \frac{3}{2}, \cdots$. This, however, gives the old Planck specific heat curve, which rises to a maximum above the equipartition value, contrary to experiment. The failure of the simple theory is doubtless due to the non-polar character of the hydrogen molecule and is probably intimately connected with the alternating intensities found in the band spectra of certain non-polar molecules.

2. The following ways of removing the specific heat dilemma are considered: (*a*) use of whole quanta, (*b*) exclusion of the state $m = \frac{1}{2}$, (*c*) exclusion of every other state in accord with the type of quantization for non-polar molecules proposed by Ehrenfest and Tolman, (*d*) "weak" quantization of every other state, (*e*) a gyroscopic molecule. Satisfactory curves are obtained with (*a*) and (*b*), but the theoretical basis on the new quantum mechanics is obscure. Hypothesis (*c*) probably gives too steep a curve and an excessively large moment of inertia, (*d*) is questionable, and (*e*) is incompatible with the diamagnetism of hydrogen. The Einstein-Bose statistics do not affect the rotational specific heat of hydrogen appreciably. Recent experimental work of Bartels and Eucken and of Schreiner shows the moments of inertia of N_2, O_2, and CO cannot be deduced from existing specific heat data and so obviates the necessity of the absurdly small moments of inertia previously required by Scheel and Heuse's measurements for these elements.

3. Recent theories of the hydrogen secondary spectrum give moments of inertia which are larger than the old values and which are hence more easily reconciled with specific heats. Ehrenfest and Tolman have suggested that the angular momentum of non-polar molecules equals only even multiples of $h/2\pi$, and according to Slater their proposal may be intimately related to the alternating intensities sometimes found in band spectra. It is shown that according to the correspondence principle the angular momentum can change by zero or $h/2\pi$ even in a non-polar molecule, provided there are simultaneous electron jumps. This fact partially destroys the quadrupolar symmetry and causes serious difficulties for their theory. The alternating intensities, however, seem difficult to explain otherwise, and may be related to the Heisenberg extension of the Pauli exclusion principle.

Croze and Dufour find that, unlike the non-magnetic Fulcher bands, certain other lines of the hydrogen secondary spectrum are resolved by a magnetic field into doublets whose displacement is comparable with the normal Lorentz value and so surprisingly large for a molecule. It is suggested that these peculiar Zeeman doublets, whose polarization is sometimes anomalous, are

due to loose coupling of the spin axis of the valence electron in either the initial or final state, but not in both.

4. The Stern-Tetrode formula for chemical constants must be modified by including terms involving the a priori probability of the lowest state and the symmetry number. If the entropy of the solid phase vanishes at the absolute zero, observed vapor pressures apparently require a whole quantum specific heat curve for hydrogen and do not allow the specific heat curve (*b*); but if we abandon the Nernst heat theorem a more general interpretation of Simon's results is simply that in hydrogen the minimum a priori probability is the same in the gaseous and solid phases. The moment of inertia 10^{-41} gm. cm^2 often deduced for the hydrogen molecule from chemical constants is erroneous. Present data on chemical constants are chaotic and the theory is uncertain owing to inadequate knowledge of the a priori probability in the solid phase and of the rôle of the symmetry number. Possibly this number is required in the solid as well as in the gas or else in neither.

INTRODUCTION

IT IS well known that the behavior of the heat capacity of hydrogen at low temperatures, where the specific heat falls below the classical value $c_p=\frac{7}{2}R$ is explained by quantizing the rotational motion of the nuclei about the center of gravity. This has been done by Reiche and other writers mentioned later in the article, using a rigid model of the molecule. An elastic model must be employed at high temperatures, since there the specific heat exceeds $\frac{7}{2}R$ because of the acquisition of quanta of nuclear vibrational motion. The resulting rotational and vibrational specific heat has been considered jointly by E. C. Kemble and the writer, and the present article can in part be regarded as an extension and revision of their paper[1] in the light of recent experimental and theoretical developments. It is now clear that the quantum theory has been revolutionized by the new mechanics developed by Born, Heisenberg and Jordan, Dirac, and Schrödinger.[2] The bearing of the new mechanics on the specific heat of hydrogen is considered in Section 1. It is there shown the specific heat data proves that in the new mechanics the hydrogen molecule cannot be quantized in the same way as a simple rotating dipole such as HCl. The failure of the simple theory is doubtless due to the non-polarity of the hydrogen molecule. In the absence of an adequate quantum theory of non-polar molecules, several speculations are given in section 2 concerning the modifications in quantization necessary to give a satisfactory specific heat curve.

[1] E. C. Kemble and J. H. Van Vleck, Phys. Rev. **21**, 653 (1923).

[2] W. Heisenberg, Zeits. f. Physik, **33**, 879 (1925); M. Born and P. Jordan, *ibid.* **34**, 858 (1925); M. Born, W. Heisenberg, and P. Jordan, **35**, 557 (1926); P. A. M. Dirac, Proc. Roy. Soc. **109***A*, 642 (1925); **110A**, 561 (1926); E. Schrödinger, Ann. d. Physik, **79**, 361, 489, 734; **80**, 437 (1926); Phys. Rev. in press.

Sections 3 and 4 consist of a discussion of band spectrum theory and chemical constants, especially in relation to the specific heat of hydrogen. Existing theories of alternating intensities in the band spectra of non-polar molecules are considered at some length as this phenomenon is doubtless intimately related to the failure of the simple (HCl type) dipole theory in explaining the specific heat of hydrogen. A digression is made to consider the unexpectedly large Zeeman separations found in certain band spectra, which we attribute to the spinning electron. The discussion in Sections 2–4 is unfortunately rather void of many definite conclusions but nevertheless represents the result of considerable labor by the author in endeavoring to correlate and criticize existing evidence and theory. It is hoped that this will at least serve to acquaint some readers with the uncertain present status of many points connected with the theory of diatomic molecules, which makes dogmatic results impossible.

Graphs of the theoretical curves obtained under various assumptions discussed in Sections 1 and 2 are deferred to Part II, in which Dr. Hutchisson correlates existing experimental data on the specific heat of hydrogen and gives the numerical results of his calculations.

1. Specific Heat of Hydrogen in the New Mechanics

By a well-known formula[3] the rotational and vibrational specific heat per gram-mol. is

$$c = R\rho^2 d^2 \ln Q / d\rho^2, \tag{1}$$

where

$$\rho = 1/kT, \quad Q = \sum_n \sum_m p_m e^{-\rho W(m,n)} \tag{2}$$

We denote by $W(m, n)$ and p_m respectively the energy and a priori probability of the stationary state of rotational quantum number m and vibrational quantum number n. We use the notation p_m rather than $p(m, n)$ inasmuch as the value of n does not influence the a priori probability. As usual, R and k denote respectively the molar and molecular gas constants. The summation in (2) is to be taken over all possible values of the quantum numbers m and n.

Value of $W(m, n)$. Throughout the article, unless otherwise stated, we shall utilize a non-gyroscopic model of the molecule, as this seems to be required by the diamagnetism of hydrogen. Up to room temperatures the specific heat can be approximately calculated with the further

[3] Eq. (1) has been given for a rigid model by Planck,[18] Reiche,[21] Tolman,[14] and many others. It is easily seen to be equivalent to Kemble and Van Vleck's Eq. (10) or to Eq. (1) of Part II.

supposition that the model is rigid. The vibrational quantum number then does not enter,[4] and the energy is

$$W(m)=(m^2h^2/8\pi^2I)+A\,, \tag{3}$$

where I is the moment of inertia and A is a constant independent of m. According to the new quantum mechanics, the rotational quantum number m is to be given the values $\frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \cdots$ in contrast to the whole quantum values characteristic of the old quantum theory. In order to make a closer connection with band spectrum notation we employ a rotational quantum number m one-half unit larger than the number j sometimes employed so that $m^2-\frac{1}{4}$ occurs in place of $j(j+1)$. This is, of course only a difference in notation, and our procedure corresponds to the Landé rather than Sommerfeld usage. That Eq. (3), with half quanta, is the proper value for the energy of a rigid rotator in the new mechanics has been shown by Heisenberg,[2] Schrödinger,[5] Mensing,[6] Dennison,[7] and others.[8] According to Schrödinger[5] the additive constant A is $-h^2/32\pi^2I$, making $W=j(j+1)h^2/8\pi^2I$ in Sommerfeld's notation. Somewhat different values of A have been proposed by Dennison[7] and others, but such differences are of no concern to us, as by Eqs. (1, 2) the additive constant in the energy does not affect the specific heat in any way.

Above room temperatures we must consider the vibrational specific heat, and it is then necessary to employ an elastic model. Also at lower temperatures the centrifugal expansion influences the specific heat to a certain degree. With an elastic model the energy W cannot be evaluated numerically until we specify the nature of the restoring force $F(r)$ for the nuclear vibrations. We have in general no knowledge concerning the form of $F(r)$ except that it must vanish as $1/r^2$, or more rapidly, for large values of r, and must be an approximately linear function of r when the nuclear separation r is close to its equilibrium value r_0. As first noted by Kratzer,[9] these requirements are conveniently met by taking

$$F(r)=a(r-r_0)/r^3. \tag{4}$$

[4] In the new mechanics there is a half quantum of vibratory energy even at the absolute zero, but, neglecting centrifugal expansion, this only adds a constant to the energy unless the temperature is so high that larger vibrational states are excited.

[5] E. Schrödinger, Ann. der Physik **79**, 489 (1926); Phys. Rev. (in press).

[6] Lucy Mensing, Zeits. f. Physik **36**, 814 (1926).

[7] D. M. Dennison, Phys. Rev. **28**, 318 (1926). Dennison's quantum numbers m, n are the same as $m-\frac{1}{2}$, σ in our notation.

[8] L. Brillouin, Comptes Rendus **182**, 374 (1926); I. Tamm, Zeits. f. Physik, **37**, 685 (1926); O. Halpern, *ibid.* **38**, 8 (1926); J. R. Oppenheimer, Proc. Cambr. Phil. Soc. **23**, 327 (1926).

[9] A. Kratzer, Zeits. f. Physik **3**, 289 (1920).

This assumption, which was used in Kemble and Van Vleck's paper[1] on vibrational specific heats, greatly simplifies the calculation and enables one to determine the energy without resorting to series developments. We do not pretend that the approximation (4) is valid for large values of $r-r_0$ but this is unnecessary since an accurate formula for large displacements is not needed in our study of specific heats. Kratzer,[9] also independently Kemble and Van Vleck,[1] showed that with (4) the energy in the old quantum theory took the very simple form

$$W(m,n)=-\tfrac{1}{2}u^{-2}h\nu_1(un+\sqrt{1+u^2m^2})^{-2}+\text{constant}, \tag{5}$$

where u is the ratio ν_1/ν_0 of the lowest quantum rotational frequency $\nu_1=h/4\pi^2I_0$ to the frequency ν_0 of infinitesimal nuclear vibrations. It is easily shown that $I_0=Mr_0^2$ and $\nu_0^2=a/4\pi^2Mr_0^3$, where $M=m_1m_2/(m_1+m_2)$ and m_1, m_2 are the masses of the two nuclei in the diatomic molecule.

In the new quantum mechanics, too, the assumption (4) (r and r_0 now being matrices) greatly simplifies the calculation, for then the energy takes exactly the same form (5) as in the old theory, except that now the rotational and vibrational quantum numbers m and n are both to be given half instead of whole quantum values. This result was proved in a recent paper by Fues[10] and has also been obtained independently by the author. We may note that without going through Fues' detailed solution of the Schrödinger wave equation, the result (5) (with half quanta) can be derived in a very simple manner by comparison of the Hamiltonian function resulting from (4) with that of a hydrogen atom. As shown by Miss Mensing,[6] the calculation of W in a central field for a given value of m is reducible to a problem of one degree of freedom by substituting $(m^2-\frac{1}{4})h^2/4\pi^2$ for the square of the resultant angular momentum. With the simplification (4) the Hamiltonian function is then

$$\frac{1}{2M}\left(p_r^2+\frac{(m^2-\frac{1}{4})\,h^2}{4\pi^2r^2}\right)-\frac{a}{r}+\frac{1}{2}\,\frac{ar_0}{r^2}+\frac{1}{2}\,\frac{a}{r_0}=W, \tag{6}$$

where matrices are written in bold-face type. Neglecting the trivial additive constant $a/2r_0$, Eq. (6) is like the Hamiltonian function for the hydrogen atom except in the numerical values of the coefficients of $1/r$ and $1/r^2$. On comparing coefficients with those for the hydrogen atom it is easily seen that the energy W for our problem can be obtained simply by substituting a for Ze^2 and $(m^2+4\pi^2ar_0Mh^{-2})^{\frac{1}{2}}$ for k

[10] E. Fues, Ann. der Physik **80**, 367 (1926). Our Eq. (5) is equivalent to combination of his Eqs. (19) and (39).

in the energy-formula of the hydrogen atom. Eq. (5) then follows on remembering that in the new quantum mechanics the energy of an H atom is still the well-known Balmer expression $-2\pi^2MZ^2e^4/(n+k)^2h^2$, except that now both the radial quantum number n and azimuthal quantum number k are half-integral.

Value of p_m. For a long time there was considerable uncertainty as to whether p_m should have the value $2m$ or $2m+1$, but the new quantum mechanics indicates very definitely that the value $2m$ ($2j+1$ in the Sommerfeld notation) is correct,[11] since in an external field with axial symmetry the axial component of angular momentum can assume the $2m$ values $-(m-\frac{1}{2}), \cdots, (m-\frac{1}{2})$. This result is required by the new mechanics for molecules (at least if polar) as well as atoms. In HCl an independent experimental proof of the a priori probability $2m$ is furnished by Bourgin and Kemble's[12] recent data on absorption intensities, and here also the half quantum numbers $m=\frac{1}{2}, \frac{3}{2}, \cdots$ are directly confirmed by Czerny's[13] measurements of frequencies in the "pure rotation" infra-red spectrum.

Failure of the simple theory. Unfortunately an impossible specific heat curve is obtained if we use the a priori probability $p_m=2m$ and half quanta[14] $m=\frac{1}{2}, \frac{3}{2}, \cdots$ to be expected from the simple theory of the rotator in the new mechanics. It is easily seen, as noted by various writers,[15,16,17] that these assumptions concerning p_m and m lead to a curve of the same type as that derived by Planck[18] with the old cell ("second") form of the quantum theory. Instead of rising gradually to the equipartition value R, the rotational specific heat with this curve ascends to a maximum about 10 percent above R and then gradually descend to the latter. No such effect is observed in hydrogen.[19] If the moment of inertia is adjusted to yield agreement

[11] The objection cited by Pauling (Phys. Rev. **27**, 568, 1926) that an a priori probability $2m$ gives the wrong sign to the temperature coefficient of the dielectric constant in HCl etc., disappears if the calculations are made by the new rather than old quantum mechanics. This has recently (Aug. 1926) been shown independently by Mensing and Pauli (Phys. Zeits. **27**, 509); Kronig (Proc. Nat. Acad. **12**, 488); and Van Vleck (Nature **118**, 226).

[12] D. G. Bourgin and E. C. Kemble, Phys. Rev. **27**, 802A (1926).

[13] M. Czerny, Zeits. f. Physik **34**, 227 (1925).

[14] The possibility of these half quanta in hydrogen was first suggested by Tolman (Phys. Rev. **22**, 470, 1923), but his calculations stressed the a priori probability $2m+1$.

[15] E. Hutchisson and J. H. Van Vleck, Phys. Rev. **25**, 243A (1925).

[16] G. H. Dieke, Physica, **5**, 412 (1925); also Phys. Rev. **27**, 639A (1926).

[17] H. Lessheim, Zeits. f. Physik, **35**, 831 (1926).

[18] M. Planck, Verh. d. D. Phys. Ges. **17**, 407 (1915).

[19] It would be interesting if measurements could be conducted at sufficiently low temperatures to see whether the anomalous maximum is found in the specific heat of

at low temperatures, the maximum would come at about 250°K whereas the specific heat observed for hydrogen is still below the equipartition value at this temperature.

2. Empirical Ways of Escaping the Specific Heat Dilemma

We are thus confronted with a serious difficulty. Since we have abundant evidence for the new mechanics, the failure of the simple theory is probably because the H_2 molecule is non-polar and so cannot be quantized in the same way as a simple rotating dipole such as HCl. Just what modifications should be made is, of course, uncertain in the absence of a detailed quantum-mechanical analysis of the electron orbits in non-polar molecules. We shall list below several specific ways of crawling out of the specific heat dilemma by assuming more or less empirically a different quantization than in the simple polar rotator. Most of the suggestions appear rather artificial and are frankly only conjectures, but one must at the same time realize that observed specific heats furnish fairly definite evidence as to what a priori probabilities and ranges of quantum numbers are legitimate. For this reason it does not appear altogether unlikely that the true specific heat curve is of the form (*b*) given below.

(*a*) *Whole quanta.* The most obvious possibility is that we still have $p_m = 2m$ but that the rotational quantum number assumes the integral values $m = 1, 2, \cdots$ instead of $\frac{1}{2}, \frac{3}{2}, \cdots$. We then get a specific heat curve calculated for a rigid molecule by Bohr[20] as early as 1916, and also independently by several other writers.[21] The computations were extended to the elastic model by Kemble and Van Vleck.[1] They show that quite satisfactory agreement can then be obtained with observed specific heats up to 2000°K provided the moment of inertia and nuclear vibration frequency are arbitrarily assigned the proper values.[22]

HCl, for we have abundant spectroscopic evidence that the simple rotator theory can be applied to HCl even though it fails in H_2. Such measurements, however, would be difficult, if not impossible, as the maximum in HCl comes at about 12°K.

H. C. Hicks and A. C. G. Mitchell have recently made an interesting attempt to calculate the specific heat of HCl from spectroscopic energy levels, but unfortunately use an a priori probability $2m+1$, Journ. Amer. Chem. Soc. **48**, 1520 (1926).

[20] N. Bohr, Abhandlungen über Atombau aus den Jahren 1913–1916. (Vieweg, 1921).

[21] E. C. Kemble, Doctor's Dissertation, Harvard University, 1917 (unpublished); F. Reiche, Ann. der Physik, **58**, 657 (1919); S. Rotszajn, *ibid.* **57**, 81 (1918).

[22] Kemble and Van Vleck used integral values for the vibrational quantum number, but Hutchisson shows in Part II of the present paper that the introduction of the half-integral vibrational quantum numbers characteristic of the new mechanics (cf. Section 1) does not alter the specific heat curves materially.

The great difficulty with the introduction of these whole quanta is that it is very doubtful whether they are allowable in the new quantum mechanics for a non-gyroscopic rotator, although Born, Heisenberg, and Jordan[2] have shown that in general the resultant angular momentum of an isolated dynamical system can be either a half or whole multiple of $h/2\pi$. By examination of the characteristic values of his partial differential equation, which is allied to the matrix theory, Schrödinger[5] is lead unambiguously to half quanta for the rotating dipole in three dimensions. Also Dennison claims that with whole quanta the transition probabilities do not fulfill the proper boundary conditions, i. e., do not vanish when the final state is impossible.[23] At the same time we must keep in mind that the hydrogen molecule is non-polar and that the low frequency part of its electrical field is that of a quadrupole rather than of a dipole (see Section 3) so that the amplitudes of the type considered by Dennison and others do not enter in radiation. It is barely possible that a quantization of a non-polar molecule with the same amount of electronic symmetry as hydrogen will yield whole quanta when the internal degrees of freedom are carefully considered. Against this possibility is the general rule advanced by band-spectrum spectroscopists[24] that whole or half quanta are to be used according as the number of electrons is odd or even.

(*b*) *Exclusion of the state* $m=\frac{1}{2}$. Another possibility is that the a priori probability is $2m$, but that the rotational quantum number m only assumes the values $\frac{3}{2}, \frac{5}{2}, \cdots$. We then get a specific heat curve of the type calculated independently by various authors[15,16,17] for the rigid molecule, and extended to the elastic model by Hutchisson. This curve is in quite satisfactory agreement with observed data. Graphs of the curves obtained for the elastic model under the assumptions (*a*) and (*b*) are given by Hutchisson in Part II, to which the reader is referred for detailed comparison of the theoretical curves and experimental values. Hutchisson shows the preference between the curves for cases (*a*) and (*b*) depends largely upon what experimental data are accepted as most accurate.

We shall see in Section 3 that some plausibility is lent to the suggestion (*b*) from a study of the Fulcher bands of hydrogen, but on the other hand it will be shown in Section 4 that the observed chemical constant of hydrogen is hard to reconcile with the idea that the hydrogen molecule has an a priori probability 3 (i. e., three different positions)

[23] Dennison, l.c. 7, p. 326.

[24] R. S. Mulliken, Proc. Nat. Acad. 12, 148 (1926).

in its state of lowest energy. It is hard to imagine any theoretical basis for the complete exclusion of the state $m=\frac{1}{2}$ without diminishing or otherwise affecting the a priori probabilities of the remaining states, though it is barely possible that some such surprising result may ensue when a detailed analysis of electron orbits in non-polar molecules is made with the new quantum mechanics and especially with the extension of the Pauli exclusion principle which is used by Heisenberg in explaining the helium spectrum, etc., and which will be briefly described on p. 1003. Use of the a priori probability $2m-1$ instead of $2m$ would automatically exclude the state $m=\frac{1}{2}$, but Hutchisson shows in Part II that the resulting specific heat curve is unsatisfactory.

(*c*) *Exclusion of every other state.* Ehrenfest and Tolman[25] have shown that in a non-polar molecule the rotational quantum number can change only infrequently and only by even multiples of $h/2\pi$, unless there are simultaneous electron jumps. For this resaon they suggest that every other value of the rotational quantum number must be excluded in a non-polar molecule. The discussion of the theory for such a procedure will be deferred until section 3, where it will be shown that the necessity of including electronic as well as nuclear transitions raises some serious difficulties, but that there is nevertheless quite possibly some analogy to the Pauli-Heisenberg exclusion principle. Irrespective of the theory we must note with Mecke[26] that there is some very strong experimental evidence in the helium band spectrum for successions of states in which every other value of the rotational quantum number is wanting, for otherwise it would be necessary to introduce the unreasonable "quarter quanta," which will be criticized in Section 3 in connection with the hydrogen and helium band spectra.

If we assume that m has the values $\frac{1}{2}, \frac{5}{2}, \frac{9}{2}, \cdots$ we are led to an impossible specific heat curve, as this supposition gives a ratio 1 : 5 between the probabilities of the two lowest state, whereas Schrödinger[27] has shown that observed specific heats demand this ratio to be about 1 : 2. Better results are obtained with $m=\frac{3}{2}, \frac{7}{2}, \frac{11}{2}, \cdots$ but even then the curve is probably too steep, as it is easily shown to be intermediate in form between the impossible Planck curve and the curve obtained under assumption (*a*), and Hutchisson shows that even the latter is rather too high at room temperatures. If we use only alternate values of m it is very likely that the state $m=\frac{1}{2}$ is wanting, as it is not found in the Curtis classification of the helium band spectrum or the

[25] P. Ehrenfest and R. C. Tolman, Phys. Rev. **24**, 287 (1924).
[26] R. Mecke, Phys. Zeits. **26**, 217 (1925); Zeits. f. Physik, **31**, 709; **32**, 823 (1925).
[27] E. Schrödinger, Zeits. f. Physik, **30**, 341 (1924).

Takahashi-Dieke interpretation of the hydrogen Fulcher bands (see section 3). We might therefore try taking $m=\frac{5}{2}, \frac{9}{2}, \frac{13}{2}, \cdots$, although this would not appear as likely as $m=\frac{3}{2}, \frac{7}{2}, \frac{11}{2}, \cdots$. With $p_m=2m$ we would then get a very good specific heat curve, as it is not difficult to show that it would be intermediate in form between the curves obtained under the assumptions (*a*) and (*b*) and these curves fall on opposite sides of some of the experimental values (see Part II). The a priori probability $2m-1$ would have the advantage of automatically excluding the state $m=\frac{1}{2}$, but the corresponding curve would probably be too steep.

If we exclude alternate values of the rotational quantum number it is necessary to employ rather large moments of intertia, viz., about[28] 7×10^{-41} gm. cm^2 with $m=\frac{3}{2}, \frac{7}{2}, \cdots$ and 9×10^{-41} with $m=\frac{5}{2}, \frac{9}{2}, \cdots$. These values appear rather large; the latter, especially is larger even than the moments of inertia deduced spectroscopically by Dieke for excited hydrogen molecules (Section 3). Also the difficulty with chemical constants mentioned under (*b*) still must be considered.

(*d*) *Diminished a priori probability for every other state.* We shall see in Section 3 with Slater[29] that the alternating intensities found in the hydrogen band spectrum furnish some evidence that every other state has a diminished a priori probability (to be contrasted with the complete exclusion of every other state under assumption *c*). Schrödinger[27] has shown that with the half quanta $m=\frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \cdots$, a satisfactory specific heat curve can be obtained by assuming the a priori probabilities of the three lowest states to be in the ratio 4 : 7 : 17 (or possibly 1 : 2 : 4) instead of the theoretical ratio 4 : 12 : 20 for the HCl-type rotator. Schrödinger's probabilities seem to have no theoretical justification, but his curves will not be very materially modified is we assume the ratio to be 4 : 7 : 20 (or 4 : 8 : 20). This might be interpreted to mean that the states $m=\frac{3}{2}, \frac{7}{2}, \cdots$ had an a priori probability $2am$ differing by a factor $a=\frac{7}{12}$ (or $\frac{2}{3}$) from those of the remaining states. This, however, does not appear likely as we have already noted that the state $m=\frac{1}{2}$ is usually wanting in the bands with alternating intensities. Another, more likely possibility, suggested to the writer by Dr. Mulliken, is the complete exclusion of the state $m=\frac{1}{2}$, and diminished a priori probabilities for $m=\frac{5}{2}, \frac{9}{2}, \cdots$.

[28] Without calculating the specific heat curves in detail we can deduce the approximate moments of inertia because observed specific heat data fix quite definitely the difference in energy between the two lowest permissible states. See Schrödinger.[27] If we excluded alternate states this energy difference would be increased unless we made an offsetting increase in the moment of inertia.

[29] J. C. Slater, Nature, April 17, 1926.

We should then have virtually a combination of (*b*) and (*d*). A satisfactory specific heat with this hypothesis does not appear altogether impossible, but calculations have not been attempted since they would be extremely arbitrary without anything to guide us on the numerical values of the ratios in the alternating sequence of probabilities. Theoretical difficulties connected with the weak quantization of every other state will be mentioned in Section 3.

(*e*) *Gyroscopic molecule.* If the molecule is gyroscopic due to an electronic angular momentum $\sigma h/2\pi$ about the axis of figure, then, as shown in fine print below, a formula for the specific heat is obtained which is the same as for a non-gyroscopic model of like moment of inertia and elasticity, except that in summing over the various states in Eq. (2) the rotational quantum number m must be given the values $\sigma+\frac{1}{2}, \sigma+\frac{3}{2}, \cdots$, instead of $\frac{1}{2}, \frac{3}{2}, \cdots$. That this is the proper range of values for m can be seen from examination of the Hönl-London amplitudes[30] for gyroscopic molecules or more directly from Dennison's matrix calculations[7] for the rigid gyroscopic molecule (his "symmetrical rotator"). The minimum value of m is greater than in the non-gyroscopic case, of course, simply because the resultant angular momentum cannot be less than the axial component thereof. It is immediately seen that a simple and tempting explanation of the ranges of values of m used in (*a*) and (*b*) is obtained if $\sigma=\frac{1}{2}$ in case (*a*) or $\sigma=1$ in (*b*), but unfortunately this is probably not the solution of the specific heat dilemma, as a gyroscopic molecule is incompatible with the diamagnetism[31] of hydrogen or with the absence of an appreciable Zeeman effect in the Fulcher bands. The latter, in fact, are not ordinarily susceptible to magnetic fields, despite the fact that according to Takahashi or Dieke (Section 3) their minimum m-value is probably $\frac{3}{2}$, indicating that the absence of the state $m=\frac{1}{2}$ is not due to the existence of a $\sigma>0$. Of course, as long as the ratio of magnetic moment to angular momentum for the internal spins of the electrons is twice the corresponding ratio for the orbital motions,[32] it is possible to have a zero magnetic moment without the logical necessity of a vanishing resultant electronic angular momentum, but a study of atomic Zeeman effect levels indicates that this situation is altogether unlikely in hydrogen. Irrespective of the diamagnetism, strong

[30] H. Hönl and F. London, Zeits. f. Physik, **33**, 803 (1925).

[31] Hydrogen is about twice as diamagnetic as helium. Cf. A. P. Wills, and L. G. Hector, Phys. Rev. **23**, 209 (1924); L. G. Hector, *ibid.* **24**, 418 (1924).

[32] E. H. Kennard, Phys. Rev. **19**, 420A (1922); also especially Uhlenbeck and Goudsmit, Naturwissenschaften **13**, 953 (1925); Nature **117**, 264 (1926).

evidence that the hydrogen molecule is non-gyroscopic is furnished by analogy with atomic spectral terms. There is increasing evidence that there is a considerable similarity in the structure of spectra of atoms and molecules with equal numbers of valence electrons.[33] Since the hydrogen molecule contains two electrons, its spectral terms should thus show some resemblance to those of alkaline earth atoms,[34] and the normal states of the latter are always S-terms without either magnetic moment or angular momentum.

Theory of specific heat of gyroscopic molecule. For a *rigid* model the equivalence of the specific heat of a gyroscopic molecule to that of a non-gyroscopic one in which the rotational quantum number is given artificially by the values $\sigma+\frac{1}{2}, \sigma+\frac{2}{2}, \cdots$ (instead of $\frac{1}{2}, \frac{2}{2}, \cdots$) is obvious. For in the new[7] as well as the old quantum mechanics the rigid gyroscopic rotator has an energy of the form $B(m^2-\sigma^2)+C$, where B and C are constants. In specific heat calculations we are interested only in the minimum value of σ and need not sum over states with larger σ since they are occupied by only a negligible fraction of the molecules at ordinary temperatures. Because σ can thus be treated as fixed, the gyroscopic effect in a rigid molecule, besides increasing the minimum value of m, only introduces an additive constant $-B\sigma^2$ in the energy, and such a constant has no influence on the specific heat.

In the case of *elastic* molecules the equivalence mentioned in the preceding paragraph can be easily established by a simple calculation. Since the exact orbits of the electrons are unknown we may allow for their gyroscopic effect by imagining a fly-wheel to be mounted on the axis joining the nuclei. If we neglect terms involving the ratio of electronic to nuclear mass no particular difficulty is introduced if we assume the moment of inertia A of the fly-wheel to be a function of r, in accordance with the fact that the size of the electron orbits doubtless depends on the nuclear separation. The nuclear restoring force is then the r-derivative of $V(r)+\sigma^2h^2/8\pi^2A(r)$ rather than of the ordinary potential energy $V(r)$, and our model of the molecule may be characterized as an elastic top with masses m_1 and m_2 at the two ends and with variable moment of inertia $A(r)$. It is found that in either the new or old quantum mechanics the energy formula is of the same form as for a non-gyroscopic model with similar radial force, except that m^2 must be replaced by $m^2-\sigma^2$. We omit the details of the calculations inasmuch as the hydrogen molecule is probably non-gyroscopic. If in particular we make the simplifying assumption (4), the expression for the energy still takes the form (5), except that the constant under the radical is $1-\sigma^2u^2$ instead of 1. This alteration is inconsequential since the energy can still be thrown into the form (5) by replacing u by $u'=u/(1-\sigma^2u^2)^{\frac{1}{2}}$ and ν_1 by $\nu_1'=\nu_1/(1-\sigma^2u^2)^2$. Such a change in the constants is of no importance for specific heats as here u and ν_1 are regarded as perfectly arbitrary. Also the difference between u, ν_1 and u', ν_1' is negligible since u^2 is the square of the ratio of the lowest rotational to the vibrational frequency, and hence $1-\sigma^2u^2$ is nearly unity.

It is interesting to note that in the ordinary mechanics the elastic gyroscopic molecule is a problem which can be treated by separation of variables, even when the moment of inertia $A(r)$ of the fly-wheel is constrained to vary with r, provided we neglect terms

[33] R. T. Birge, Nature, **117**, 300 (1926); F. Hund, Zeits. f. Physik, **36**, 657 (1926); R. Mecke, *ibid.* **28**, 261 (1924); Naturwissenschaften, **13**, 698, 755 (1925); R. S. Mulliken, Phys. Rev. **26**, 1, 561 (1925); Proc. Nat. Acad. **12**, 144 (1926); J. W. Nicholson, Phil. Mag. **50**, 650 (1925).

[34] Cf. Mulliken, Proc. Nat. Acad. **12**, 338 (1926).

[35] M. Born, die Naturwissenschaften, **10**, 677 (1922).

involving the ratio of the electronic to nuclear mass. The coordinates to be used are the nuclear separation r and a set of Eulerian angles θ, φ, ψ giving the position of the axis of figure and amount of rotation of the fly-wheel about same. By setting up the Lagrangian function one finds that the angular momentum $p_\psi = A(\dot{\psi} + \dot{\varphi}\cos\theta) = \sigma h/2\pi$ of the fly-wheel is constant. Because of this and the fact that the angular momentum of the nuclei is perpendicular to that of the fly-wheel, the interesting result is obtained that the axis of figure precesses regularly about the invariable axis of angular momentum and there is no nutation despite the oscillations in the nuclear separation and radius of the fly-wheel. This is also true in the new mechanics.

The crossed-orbit model of the hydrogen molecule. At this point we may note that in the old quantum theory we would have $\sigma = 1$ if we assumed a model of the hydrogen molecule proposed by Born[35] which is the natural analog of the Bohr-Kemble crossed-orbit model of the normal helium atom (to be contrasted with the early Bohr circle model which had $\sigma = 2$). This crossed-orbit model[36] has a good deal of dynamical simplicity and symmetry, but is incompatible with the diamagnetism of hydrogen.[37] A calculation of the energy and moment of inertia of the crossed-orbit model of the hydrogen molecule has been made by E. Hutchisson with the old quantum theory and will be published in the PHYSICAL REVIEW. His calculations yield a much greater work of ionization than is observed, and a moment of inertia 4.9×10^{-41} gm cm^2 which is larger than the estimates 1.98×10^{-41} and 2.99×10^{-41} deduced from specific heat curves with assumptions (a) and (b) respectively. These discrepancies are, of course, not surprising since the results with the new mechanics are doubtless different. We had originally intended to make the crossed-orbit model the central point of the discussion in the present article but have now relegated it to a subordinate position since in the new mechanics the normal hydrogen molecule is probably non-gyroscopic, although in other respects it may show a limited amount of resemblance to the crossed-orbit model of the old theory.

Einstein-Bose statistics immaterial. In a conversation with the writer, Dr. Kramers raised the question whether the rotational specific heat might not be modified at low temperatures by employing the Einstein-Bose statistics,[38] for which the evidence is accumulating. It is well known that according to this new statistics the Maxwell distribution of translational velocities is modified at very low temperatures, and Jordan[39] has indicated that there is a corresponding departure from the Boltzmann distribution formula for determining the distribution of atoms or molecules among a discrete succession of quantized states, as a factor $1/(e^{A+W/kT}-1)$ occurs in place of $e^{-A-W/kT}$. The specific heat equation (1) based on the Boltzmann distribution formula is then no longer applicable. This fact, however, cannot be the solution of the specific heat difficulty, for the corrections to (1) are entirely insigni-

[36] For further description and discussion of this model, with references, see J. H. Van Vleck, "Quantum Principles and Line Spectra" (Bull. Nat. Research Council No. 54), Chap. VII, especially p. 90.

[37] Cf. Van Vleck, l.c.,[36] p. 99.

[38] We shall not attempt to explain the theory of the new statistics. See N. Bose, Zeits. f. Physik **26**, 178 (1925); A. Einstein, Berlin Acad., 1924, 261; 1925, 3, 18; also summary in A. Landé, "Die Neuere Entwicklung der Quantentheorie," 2nd Ed., p. 126.

[39] P. Jordan, Zeits. f. Physik **33**, 649 (1925).

ficant except at temperatures which are so low that the rotational specific heat has dropped to practically nil in hydrogen. The reason why the ordinary statistics can be employed in calculating specific heats is simply that the temperature and pressure range is such that two or more molecules seldom crowd into the same cell of the phase space, so that the Einstein-Bose interference effcts do not enter appreciably. A simple calculation [40] indicates that the modifications will first become appreciable when the quantity $\chi=(2\pi mkT)^{3/2}V/h^3N$ (which is of the order of magnitude of e^A unless A is very small) is comparable with unity. Here m is the mass of the molecule, and N/V is the no./cc. Now even at a temperature as low as 30°K, at atmospheric pressure we still have $\chi>10^2$ so that the modifications are very small. This as what we should expect since no large "degeneration" of any gas has yet been observed experimentally.

Specific Heats of N_2,O_2,CO. We now digress to revise a previous attempt of Kemble and Van Vleck [1] to calculate the moments of inertia of N_2,O_2, and CO from specific heat data. In Scheel and Heuse's original paper the conclusion was reached that the specific heats of these gases fell appreciably below the equipartition value $c_p=\frac{7}{2}R$ at 92°K. Kemble and Van Vleck found that absurdly low moments of inertia were necessary to explain this result. Consequently they suggested as one possibility that the values given by Scheel and Heuse [41] for specific heats in the ideal gas condition might be too low because of an incorrect reduction to zero pressure of the measurements made at one atmosphere. Investigations of Bartels and Eucken [42] on the equation of state of nitrogen at low temperatures, of which Kemble and Van Vleck were not aware, indicate that this is indeed the case. Bartels and Eucken find the Berthelot equation of state employed by Scheel and Heuse is inaccurate at low temperatures, and they conclude that the specific heats of N_2,O_2, and CO are probably normal at 92°K. This is substantiated by recent experiments of Schreiner [43] who finds that

[40] Cf., for instance, Landé, l.c.,[38] p. 132. Because the internal vibrational and rotational degrees of freedom must be added to those of translation, our phase space is 12 instead of 6-dimensional. However at low temperatures and also in calculating the order of e^A at higher temperatures, we may consider all molecules to be in their lowest rotational and vibrational state. We then have virtually a 6-dimensional problem, except that the a priori probability of the lowest state and Ehrenfest-Trkal symmetry number will enter as factors (cf. §4) but these factors will clearly not change orders of magnitude.

[41] Scheel and Heuse, Ann. der. Physik **40**, 473 (1913).

[42] R. Bartels and A. Eucken, Zeits. f. Phys. Chem. **98**, 70 (1921).

[43] E. Schreiner, *ibid.* **112**, 1 (1924).

the specific heats of these gases conform to the classical theory even at 60°K. The moments of inertia of N_2,O_2, and CO thus cannot be calculated from existing specific heat data.

3. Relation to Band Spectra

It is essential that the theoretical interpretation of the specific heat of hydrogen be consistent with that of its band (secondary) spectrum. This requirement of consistency may furnish some light on what values for the moment of inertia and nuclear vibration frequency can legitimately be assumed in calculating specific heats and also whether half or whole quanta should be employed.

Moments of inertia. Here we must remember that excited states have larger orbits and hence ordinarily greater moments of inertia that normal states. Consequently we may expect the analysis of visible band spectra to set only an upper limit to the moment of inertia which it is permissible to use in specific heats.

Whole quanta were employed in Lenz's[44] early interpretation of the Fulcher bands of hydrogen, yielding a moment of inertia about 1.85×10^{-41} gm. cm.^{2}. After the advent of half quanta it was shown by Allen[45] and Curtis[46] that better results could be obtained if the rotational quantum number m were also given the values $\frac{1}{2}, \frac{3}{2}, \cdots$. In consequence of this and especially of the well-known success of half quanta in HCl it has been commonly supposed that the values $\frac{1}{2}$, $\frac{3}{2}, \cdots$ should be used in the specific heat of hydrogen, but we have seen that this is not consistent with experimental data unless we assume the rather unlikely a priori probabilities given in (*d*), Section 2. Irrespective of this fact, another difficulty confronting the Allen-Curtis interpretation of the Fulcher bands is that it gives a smaller moment of inertia than does specific heats. The moment of inertia 1.4×10^{-41} deduced from specific heats by Tolman[14] and Schrödinger[27] under the assumption $m=\frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \cdots$ is considerably smaller than the value 1.98×10^{-41} obtained with whole quanta (case *a*, Section 2) or 2.99×10^{-41} obtained with exclusion of $m=\frac{1}{2}$ (*b*, Section 2). This fact has frequently been cited[47] as an argument favoring the half-quanta $m=\frac{1}{2}, \frac{3}{2}, \cdots$ in specific heats, but even the value 1.4×10^{-41} is larger than one of

[44] W. Lenz, Verh. d. D. Phys. Ges. **21**, 632 (1919). See also M. Kiuti, Proc. Phys.-Math. Soc. Japan (3) **5**, 9 (1923).

[45] H. S. Allen, Proc. Roy. Soc. **106A**, 69 (1924).

[46] W. E. Curtis, *ibid.* **107A**, 570 (1925). Like Allen, Curtis uses both half and whole quanta. The main difference between their interpretations is that the half and whole quantum states are transposed.

[47] Cf., for instance, Tolman,[14] Schrödinger,[27] Lessheim.[17]

the moments of inertia 1.25×10^{-41} deduced from band spectra by Curtis[46].

An interpretation of the Fulcher bands totally different from that of Lenz, Kiuti, Allen and Curtis has been proposed by Takahashi[48] and also independently by Dieke.[49] With the latter authors the rôles of vibrational and rotational quantum numbers are interchanged, the latter being indentified with Allen's "vertical" rather than "horizontal" series. The most important bands become "Q" rather than "P" or "R" branches,[50] and the rotational quantum number is given only the values $\frac{3}{2}, \frac{5}{2}, \cdots$, excluding the state $m=\frac{1}{2}$ and suggesting possibility (b), Section 2. The interpretation proposed by Takahashi and Dieke is probably preferable to the other viewpoints mentioned in the preceding paragraph. In the first place it is most natural to identify successive rotational quantum numbers with the "vertical" series and vibrational quantum numbers with the "horizontal," rather than vice versa, for the frequency differences between successive terms of the vertical series are smaller than those of the horizontal. Also moments of inertia are obtained which are larger than the values used in specific heats, as should be the case. Dieke derives the moment of inertia 8.2×10^{-41} for some of the excited states, while Takahashi gets the even larger value 2×10^{-40}.

The classification of lines in the hydrogen secondary spectrum has been greatly extended through the researches of Richardson and Tanaka,[51] Sandemann,[52] and Curtis.[53] Most of the moments of inertia deduced by Richardson and Tanaka are smaller than the values required by (a) or (b), Section 2, and one, at least, of their moments of inertia is smaller even than that with (d), Section 2. This may be a serious difficulty, for Richardson's classification includes a large number of lines not comprised in the Fulcher bands and so not included in the ordinary Takahashi-Dieke scheme. Fortunately, however, Richardson has just published another paper[54] in which he gives a large numer of

[48] Y. Takahashi, Jap. Journ. of Phys. **2**, 95 (1923).

[49] G. H. Dieke, Proc. Amsterdam Acad., **27**, 490 (1924). Dieke's interpretation of the relations between the constants in the band spectrum differs from Takahashi's in some respects.

[50] We use the terminology of band spectroscopists, who call a spectral series of the "P" or "R" type if the rotational quantum number increases or decreases by unity in emission, and of the "Q" type if it is unaltered.

[51] Richardson and Tanaka, Proc. Roy. Soc. **107A**, 602 (1925); also Richardson, *ibid.* **108A**, 553; **109A**, 35, 239 (1925).

[52] I. Sandemann, *ibid.* **108A**, 607 (1925); **110A**, 326 (1926).

[53] W. E. Curtis, Phil. Mag. **1**, 695 (1926).

[54] O. W. Richardson, Proc. Roy. Soc. **111A**, 714 (1926); Nature, **118**, 116 (1926).

important new series relations which are intimately related to those of Takahashi and Dieke, and which can, in fact, partly be regarded as extensions of the latter. Previously missing P and R branches are supplied, etc. Richardson gives a new method of estimating the moment of inertia which is perhaps more accurate than those of Takahashi or Dieke. It gives moments of inertia mostly between 3×10^{-41} and 4×10^{-41}, or larger than any of the values deduced from specific heats in Section 2 except in case (c), in which every other rotational state is excluded. These recent developments are perhaps especially favorable to a curve of the type (b), Section 2, which yields a moment of inertia 2.99×10^{-41}. The new Richardson series relations seem to require at least a partial abandonment of some of the rotational classifications given in previous articles by Richardson[51] and Tanaka,[51] and possibly the revision is so complete that the difficulty of low moments of inertia is entirely avoided. At any rate the hydrogen secondary spectrum is so complicated and difficult to interpret that it does not as yet appear to furnish any conclusive evidence against any of the various specific heat curves enumerated in Section 2 except that case (c) probably requires an excessively large moment of inertia.

Nuclear vibration frequency. It is quite probable, however, that spectroscopists of the ultra-violet will soon be able to supply the moment of inertia of the normal state of the hydrogen molecule and so definitely determine the correct value for use in calculating specific heats. Ultra-violet measurements made by Witmer[55] have already furnished the value 1.277×10^{14} sec^{-1} for the normal nuclear vibration frequency which agrees almost exactly with that used in curve (b). The relation of this value to that deduced from specific heats is discussed by Hutchisson in Part II.

Alternating intensities and the correspondence principle. A curious phenomenon encountered in the band spectra of non-polar molecules is that consecutive lines of series generated by varying the rotational quantum number are sometimes alternately weak and strong in intensity. Such anomalies are apparently found in the "vertical" series of the Fulcher bands. As noted by Dieke,[56] this fact must be regarded as a strong argument for the Takahashi-Dieke interpretation of these bands, since the alternations in intensities are always a rotational rather than vibrational effect. An adequate theoretical explanation of the alternating intensities has yet to be given. Very likely, as suggested by Slater,[29] this phenomenon is ultimately ascribable to the fact that

[55] E. E. Witmer, Proc. Nat. Acad. **12**, 238 (1926).
[56] G. H. Dieke, Zeits. f. Physik **32**, 180 (1925); Phil. Mag. **50**, 173 (1925).

nuclei in non-polar molecules radiate like a quadrupole rather than a dipole. Slater's suggestion is intimately related to a modification in the quantum conditions for non-polar molecules suggested by Ehrenfest and Tolman,[25] whose theory is based on the correspondence principle and is explained in the following paragraph.

In the classical theory the electric field at a large distance R from the molecule is shown by Page[57] and others to be

$$E=\frac{1}{Rc^2}\left[\left\{\frac{d}{dt}(\sum qv)+\frac{1}{c}\frac{d^2}{dt^2}\sum(qr\cdot Mv)+\cdots\right\}\times M\right]\times M \quad (7)$$

where M is a unit vector in the direction of the radius R and where r and v are respectively the position and velocity vectors of the charge q. The summation is to be taken over all the charges in the system. If we wish to consider only the rotational motion of the electrons and do not attempt to analyze the motion of the electrons, we may use the so-called "dumb-bell" model of the molecule, which consists of two rigidly-connected point charges rotating in a common plane about their center of gravity. The summation $\sum$ in (7) then consists of only two terms. In polar molecules, such as HCl, the two ends of the dumb-bell are different. The first order term $\sum qv$ then does not vanish and has the same frequency ω_m as a rotation of the molecule or dipole through 360°. In a non-polar molecule, however, the two ends of the dumb-bell are identical and the two nuclei make equal and opposite contributions to $\sum qv$. The molecule may then be termed a "quadrupole" and a rotation through 180° will give a configuration indistinguishable from the initial one. Since $\sum qv$ vanishes, the nuclear radiation is to a first approximation zero in a non-polar molecule. If, however, we consider terms in E of the order $1/c^3$, there will be a small amount of radiation whose frequency is that of a rotation through 180°. This follows since in the symmetric dumb-bell the term $\sum(qr\cdot Mv)$ does not vanish and is easily seen to have the frequency $2\omega_m$. Consequently the effective frequency is twice that for the polarized molecule and identified with a change in angular momentum of amount h/π rather than $h/2\pi$, since by the correspondence principle the octave of a frequency is associated with a change of two units in the corresponding quantum number. Therefore Ehrenfest and Tolman tentatively suggest that in a non-polar molecule the fundamental period is $1/2\omega_m$, and that correspondingly the proper quantized values for the angular momentum are 0, h/π, $2h/\pi$, $3h/\pi$ instead of 0, $h/2\pi$, h/π, $\cdots$ so that compared with a polar molecule every other rotational state is

[57] L. Page, Phys. Rev. 20, 18 (1922).

missing.[58] Here and elsewhere in the following discussion we assume for brevity that the lowest allowed value of the angular momentum is zero. Actually because of the half quanta characteristic of the new quantum mechanics it is likely either $\frac{1}{2}h/2\pi$ or $\frac{3}{2}h/2\pi$ (in the Landé notation), but can fictitiously be made zero through changing the origin for measuring angular momentum. This is legitimate for our purposes as the inclusion in the angular momentum of an additive term $\frac{1}{2}h/2\pi$ or $\frac{3}{2}h/2\pi$ common to all stationary states does not affect the essential nature of our conclusions.

Miscellaneous considerations relating to Ehrenfest and Tolman's suggestion. In order for the nuclear radiation to vanish to a first approximation, it is essential that the two nuclei have equal masses as well as equal charges, for otherwise the center of rotation is not equidistant from both nuclei. Hence we may have a pure rotation spectrum emitted by a non-polar molecule whose two nuclei are different isotopes of the same element. Such a spectrum, however, would obviously be faint even though it arises from the first order terms in (7).

In Ehrenfest and Tolman's paper it is assumed that the nuclei rotate in one and the same plane. This assumption is not valid in a gyroscopic molecule, for here the invariable axis of angular momentum is no longer normal to the line joining the nuclei. Hence a rotation through an angle 360° rather than 180° about the invariable axis is required to bring the nuclei back to a configuration indistinguishable from the initial one. So we see that in the second order radiation from a gyroscopic molecule the angular momentum can change by $h/2\pi$ as well as h/π. In fact, it is not difficult to work out the Fourier expansion of the nuclear part of the second term of (7) for gyroscopic molecules. It contains trigonometric terms in both $2\pi\omega_m t$ and $4\pi\omega_m t$ and of comparable amplitude for low values of the rotational quantum number m. For high temperatures and large values of m the invariable axis is nearly normal to the line joining the nuclei. Then the term in $4\pi\omega_m t$ has much the larger amplitude and changes in angular momentum of amount h/π should be more common than those of amount $h/2\pi$. In this connection it may be noted that every other state appears to be wanting in certain series of the oxygen band spectrum,[26] though the experimental evidence is somewhat uncertain. In view of the above, this result is rather surprising, for the oxygen molecule is paramagnetic and so likely gyroscopic. Alternations might, however, arise from the low amplitude rather than complete absence of the terms in $2\pi\omega_m t$.

It may be noted that when the angular momentum changes by h/π due to second-order effects, the radiated wave-train cannot have the ordinary circularly-polarized structure associated with radiation from a rotating Hertzian dipole. In fact Rubinowitz and Bohr have shown that the angular momentum of any ordinary elliptically polarized spherical wave-train of energy $h\nu$ cannot exceed $h/2\pi$ (Cf. Sommerfeld, Atombau, Eng. Ed., App. 9). Instead we have a spherical wave of an entirely different type whose structure can be worked out with classical electrodynamics from the second term in (7).

The writer believes that a serious objection to the above conclusions of Ehrenfest and Tolman is the fact that they do not consider the effect

[58] We assume a diatomic molecule throughout the discussion. Ehrenfest and Tolman show that in the more general case of any polyatomic molecule the analogous proposition is that the angular momentum changes by $\sigma h/2\pi$ and equals only integral multiples of $\sigma h/2\pi$, where σ is the Ehrenfest-Trkal symmetry number to be explained in Section 4.

of the electronic motions on the multiple Fourier expansion of the electrical moment of the atom. Although the electrical moment of a symmetric molecule is zero when averaged over the periods of the electrons, it is not instantaneously zero. It may, for instance, happen that one electron rotates about the axis joining the nuclei in a larger orbit than the "inner electrons", which presumably form some sort of "closed configuration".[59] There is then an instantaneous electrical moment which rotates rapidly about the line joining the nuclei. In fact we may expect that in general the multiple Fourier expansion of the electrical moment $p=\sum qr$ of a diatomic molecule is of the form

$$\begin{aligned} p_x+ip_y &= \sum A(\tau_1, \cdots, \tau_f, \tau) \exp. 2\pi i(\tau_1\omega_1+\cdots+\tau_f\omega_f+\tau\omega_n+\omega_m)t, \\ p_z &= \sum B(\tau_1, \cdots, \tau_f, \tau) \exp. 2\pi i(\tau_1\omega_1+\cdots+\tau_f\omega_f+\tau\omega_n)t, \end{aligned} \tag{8}$$

where $\omega_1, \cdots, \omega_f$ are the electronic frequencies, ω_n is the frequency of vibration along the line connecting them, and ω_m is the frequency of a complete (360°) rotation of the molecule about its axis of resultant angular momentum, which we take as the z-axis. We shall denote by $n_1, \cdots, n_f, n, m$ the quantum numbers associated respectively with the frequencies $\omega_1, \cdots, \omega_f, \omega_n, \omega_m$. The summation in (8) is with respect to the integers $\tau_1, \cdots, \tau_f, \tau$ and extends in general from $-\infty$ to $+\infty$ for each integer. In non-polar molecules the terms are to be excluded for which $\tau_1=\tau_2=\cdots=\tau_f=0$, for in such molecules the average electrical moment in any direction is zero on averaging over the electronic periods. Hence in non-polar molecules there cannot be an appreciable vibrational or pure rotational spectrum in which the electronic quantum numbers $n_1, \cdots, n_f$ are unaltered, though there is, of course, still the second-order quadrupolar radiation discussed in the preceding paragraph. The amplitudes in (8) associated with combination overtones involving the electronic frequencies need not, however, vanish, and therefore there can be an "electronic spectrum" due to alterations in the electronic quantum numbers $n_1, \cdots, n_f$ along with which there may be a change in the vibrational quantum number n and a zero or unit change in the rotational quantum number m. Hence *even in a non-polar molecule the angular momentum may change by either* 0 *or* $h/2\pi$ *provided there are simultaneous changes in the electronic quantum numbers.* This point has been mentioned in connection with

[59] Several examples of "one-valence-electron emitters of band spectra" have been given by R. S. Mulliken, Phys. Rev. **26**, 561 (1925).

the hydrogen molecule-ion by Niessen[60] and Pauli,[61] neither of whom, however, introduce the Ehrenfest-Tolman type of quantization.[62]

It is seen that Ehrenfest and Tolman's suggestion that the angular momentum be only even multiples of $h/2\pi$ can be accepted as valid only if the second-order nuclear transitions have a much more important effect on the quantization that the first order electronic transitions. We call the transition of the first or second order according as it results from the first or second term in (7). It is obviously impossible for all electronic levels to have angular momenta which are even multiples of h/π, for the rotational quantum number can change by unity in the emission or absorption of electronic spectra. It is, however, conceivable that certain electron levels might have only even angular momenta, others odd angular momenta and still others perhaps both even and odd angular momenta. Here for brevity we measure the angular momentum in multiples of the quantum unit $h/2\pi$. We would then have only "P" and "R" branches connecting even and odd levels, and only a "Q" branch connecting two even or two odd levels.[50] In passing from an initial state with both even and odd angular momenta to an even final state, the "Q" and "P, R" lines would alternate as the initial rotational quantum number becomes progressively even and odd.

[60] K. F. Niessen, Zur Quantentheorie des Wasserstoffmolekul-Ions (Dissertation Utrecht, 1922).

[61] W. Pauli, Jr., Ann. der Physik **68**, 238 (1922).

[62] Our discussion is based on the multiple Fourier series of the classical theory rather than the matrices of the new quantum mechanics because this is simpler and does not affect the general trend of our conclusions if we use the correspondence principle as our guide. However, we must note that sometimes the electrons in the molecule might classically be so symmetrical that all the amplitudes in (8) vanish, making the electrical moment even instantaneously zero. This situation would be particularly likely to occur in the normal state. A simple example is furnished by the old Bohr circle model of the helium atom, in which the two electrons are at opposite extremities of a diameter. At first thought we might think that there would then be no electronic combination overtones to complicate the Ehrenfest-Tolman method of quantization, but we must take into account the fact that in employing the correspondence principle we must consider both the initial and final states (as well as intermediate orbits) and excited orbits will in general be less symmetric than the normal one. It is thus probably legitimate in the old quantum theory to take the electronic angular momentum of the crossed-orbit model of the hydrogen molecule or helium atom to be $h/2\pi$ rather than an even multiple of $h/2\pi$ despite the fact that in these models a rotation of the two electrons through only 180° about the axis of symmetry brings the system back to a configuration indistinguishable from the initial one.

In the new quantum mechanics it is still more apparent that the electron transitions will disturb the quadrupolar symmetry even in the most symmetric models. For when matrices are employed there will always be terms (matrix elements) of finite amplitude involving zero or unit changes in the rotational quantum number since there are always possible transitions to excited electron states.

This seems decidedly hard to reconcile with the correspondence principle, as with any simple application of the latter the "P", "Q", and "R" branches should by (8) occur simultaneously, whereas with the scheme just indicated it has been necessary to rule out either "P" and "R" or "Q" branches to avoid transitions to non-existent states. Nevertheless we shall see that the helium band spectrum furnishes evidence for this peculiar type of structure in which alternate rotational states are missing. Similarly the oscillatory intensities found in certain band spectra can be heuristically explained by assuming that because of the Ehrenfest-Tolman effect the statistical weights or a priori probabilities of even states are less than those of the odd, or vice versa. This is the essence of the suggestion recently made by Slater.[29] How this procedure is to be reconciled with the correspondence principle is not clear because of the considerations mentioned above, and Slater's idea would scarcely appear probable were not the experimental evidence so difficult to explain otherwise. As mentioned to the writer by Professor Bohr, a serious difficulty is the fact that if initial even and odd states are equally probable, but if the final even and odd states are of unequal weight, then the transition probabilities would have to be alternately large and small, scarcely in line with the simple correspondence principle.

At the absolute zero all the molecules may be assumed to have zero angular momentum (with our normalization of additive constants). As the temperature is increased states of larger angular momentum can be reached by (*a*) collisions with other molecules or atoms, (*b*) second order absorption of pure rotational quanta, or (*c*) first order absorption of electronic quanta, followed by a similar emission in which the change of angular momentum is not the reverse of that in absorption. Here the quanta associated with the frequency ω_m in (8) are termed "pure rotational", while the quantum numbers associated with $\omega_1, \cdots, \omega_f$ are termed "electronic". The mechanism (*a*) is probably the most important at ordinary pressures, for here collisions between molecules are frequent compared to the average time intervals between the absorption of quanta of radiation. Ehrenfest and Tolman suggest the mechanism (*b*), whereby molecules can reach only states whose angular momenta are even multiples of $h/2\pi$. A simple calculation may be made to estimate the relative importance of (*b*) and (*c*). This shows[63] that the second order rotational transitions are about

[63] The calculation is considerably simplified by Tolman's observation (Phys. Rev. **26**, 431, 1925) that absorption probability coefficients are approximately determined by the size of the orbit rather than the frequency, and so have approximately the same

$v^2\rho(\nu_m)/c^2\rho(\nu_e)$ as probable as first order electronic transitions, where v is the nuclear velocity, $\rho(\nu)$ is the energy density, and ρ_m, ρ_e are respectively the frequencies associated with the rotational and electronic transitions. Using the Planck value of $\rho(\nu)$, and taking the moment of inertia $I=2\times10^{-41}$ gm. cm^2 and $h\nu_e=11.1$ volts, one of the resonance potentials in molecular hydrogen, we readily find that a temperature of about 3,000 degrees must be reached before the number of first order electronic transitions (c) is comparable to that of second order rotational transitions (b), while at a temperature of 100° K, such as enters in the study of specific heats, the process (b) is 10^{500} more probable than (c). The relative preponderance of the second order rotational transitions suggests that they exert the dominating influence on the quantization at low temperatures, where it might be asumed that the electron transitions are ineffective in so far as the quantum conditions are concerned. We might then have a case of "weak quantization"[64] whereby the a priori probability of the states of odd rotational quantum number is diminished at low temperatures. This, however, is questionable. We have seen in (d), Section 2 that the complete exclusion of every other state probably does not give a good specific heat curve and requires an excessively high moment of inertia. Also an a priori probability invariant of the temperature is basic to the Einstein derivation of the Planck radiation formula, and if there were a variation of the a priori probability, there would have to be a change of the transition probability coefficients with temperature, which is hard to reconcile with the correspondence principle. In bands with alternating intensities, the intensity ratio of the strong to the weak lines is found experimentally to be a small number (always less than ten), whereas with the weak quantization hypothesis in its most naïve form one would presumably expect this number to very large (or infinite in case alternate terms are entirely excluded). Nevertheless there seems to be experimental evidence that the oscillating intensities are due to (I) alternations in statistical weights, for otherwise it would be necessary to attribute them to (II) alternations in transition probabilities or to (III) overlapping of two distinct bands which give respectively the weak and strong lines. Against the possibility (II) Slater[29] notes

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value for first order rotational transitions (when present) and first order electronic transitions. The factor v^2/c^2 results from the fact that the second order transitions are of this order compared to the first order ones, while the factor $\rho(\nu_m)/\rho(\nu_e)$ comes from the fact absorption is proportional to the energy density.

[64] For theoretical discussions of "weak quantization," see ref. 25; also Ehrenfest and Breit, Zeits. f. Physik, 9, 207 (1922); J. C. Slater, Phys. Rev. 26, 419 (1925).

that lines with a common initial state are either all weak or all strong, presumably indicating that paucity of molecules in the original state (i.e. low statistical weight) rather than low transition probabilities are the cause of weakness, unless one makes the hypothesis that *all* transition probabilities associated with certain initial states are weakened. The hypothesis (III) has been made by Bury[65] in the Fulcher bands of hydrogen, but appears objectionable because it leads to quarter quanta in the helium band spectrum, which we shall see are untenable.

Relation to the Pauli-Heisenberg exclusion principle. It appears quite certain that the oscillations in intensity are somehow ascribable to the quadrupolar symmetry of non-polar molecules. Definite experimental evidence is furnished by the often-noted fact that the alternating intensities are found only in non-polar molecules. Slater's suggestion must thus be regarded as correct in a general way, even though we have seen that there can scarcely be a "weak and strong" quantization of the ordinary type proposed by various authors in the old quantum theory. As suggested to the writer by Professors Bohr, Kramers, and Born, and also by Heisenberg himself, it appears likely that the alternating intensities are in some way connected with the extension of the Pauli exclusion principle which has recently been developed by Heisenberg in applying the new quantum mechanics to the spectrum of neutral helium and to the differences between singlet and triplet spectra. Pauli[66] showed that it is necessary to exclude stationary states in which two or more electrons have identical sets of quantum numbers. Heisenberg[67] finds it is also necessary to exclude all stationary states which can combine spectroscopically with those excluded by Pauli. Heisenberg's extension of the Pauli rule debars complete spectral systems, as for instance a parhelium triplet system and orthohelium singlet system, neither of which have ever been observed. Possibly application of the Heisenberg procedure to non-polar molecules will exclude alternate rotational states in the cases (such as the helium band spectrum) where every other line is observed to be missing. At any rate one may tentatively assume that anomalous intensities are found in non-polar molecules because their high degree of symmetry

[65] C. R. Bury, Phil. Mag. **50**, 1139 (1925). Bury uses whole quanta, whereas the half quanta used by Takahashi and Dieke are probably more satisfactory. The half quanta appear to remove the oscillating deviations in frequency noted by Bury and so may destroy perhaps the main argument for the hypothesis (III).

[66] W. Pauli, Jr., Zeits. f. Physik, **31**, 765 (1925).

[67] W. Heisenberg, *ibid.* **38**, 411 (1926).

necessitates exclusions by the Pauli-Heisenberg rule. It is to be hoped that the exclusion principle will lessen the intensity of every other line, rather than obliterate it entirely, in the more common instances where alternate lines are found experimentally to be weak instead of entirely missing. It is not clear whether this effect is more likely to result through the exclusion principle cutting down the statistical weight of every other state or through its diminishing the transition probabilities of all lines having a common origin at such a state. Definite answers cannot, of course, be given until a method is found for applying the new quantum mechanics to the general non-polar molecule.

Quarter quanta and the Kramers-Pauli Model. A quite different attempt to explain alternating intensities is found in the quarter quanta hypothesis of Dieke.[68] It is based on the formula $(m\pm\epsilon)^2h^2/8\pi^2I$ which Kratzer[69] and also Kramers and Pauli[70] have derived for the energy of a molecule possessing an electronic angular momentum $\epsilon h/2\pi$ normal to the axis of figure. The sequence of energy levels for the ordinary rotator with $\epsilon=0$ and half integral values of the rotational quantum number is obviously the same as that given by the Kramers-Pauli formula when in the latter we take ϵ to be $\frac{1}{4}$, m to be integral, and the moment of inertia I to be one fourth as large as in the simple rotator. The effective quantum number $m\pm\epsilon$ is then a "quarter integer." The values $\frac{3}{4}, \frac{7}{4}, \cdots$, correspond to parallel nuclear and electronic angular momenta, and $\frac{1}{4}, \frac{5}{4}, \cdots$, to anti-parallel. The alternating intensities are attributed by Dieke to the fact that the statistical weights are different in the parallel and anti-parallel cases, but this effect probably does not give as pronounced alterations as are observed experimentally.[71]

It is altogether probable that quarter quanta must be discarded for a variety of reasons. In the first place it requires half rather than whole unit changes in the effective quantum number $m\pm\epsilon$ in the emission of the "P" and "R" branches, and this is hard to reconcile with the correspondence principle.[26] Another difficulty is that Kramers and Pauli[70] have shown the motion is unstable in the anti-parallel case.

There are, furthermore, serious dynamical objections to the Kramers-Pauli model with $\epsilon\neq0$. In such a model it is assumed that when the nuclei are at rest there is a stationary component $\epsilon h/2\pi$ of electronic

[68] G. H. Dieke, Zeits. f. Physik **31**, 326 (1925).

[69] A. Kratzer, Münchener Akad. p. 107 (1922).

[70] H. A. Kramers, Zeits. f. Physik **13**, 343 (1923); H. A. Kramers and W. Pauli, Jr., *ibid.*, **13**, 351.

[71] This is noted by Dieke himself in connection with Hulthen's data in nitrogen (Zeits. f. Physik **33**, 167, 1925, footnote).

angular momentum which is normal to the axis of figure. Miss Mensing[72] shows that actually, except with unlikely special orbital arrangements, the forces exerted by the nuclei will cause the normal component of angular momentum to precess[73] rapidly about the axis of figure. There is, in fact, a rough similarity to the familiar precession of a gyroscope in a gravitational field. Owing to the precession, the average electronic angular momentum in any direction normal to the axis of figure vanishes on the average, and from this it is easily shown that, neglecting additive constants, the energy due to nuclear rotation is very approximately $m^2h^2/8\pi^2I$ instead of $(m\pm\epsilon)^2h^2/8\pi^2I$. Miss Mensing used the conventional mechanics, and Hund[33] states that in the new quantum dynamics there are not even special solutions in which $\epsilon\neq 0$. Consequently in the discussion of quantization and specific heats in Sections 1 and 2 we have not introduced an electronic angular momentum $\epsilon h/2\pi$ normal to the axis of figure, even though such an addition obviously introduces no particular difficulty in the calculation, at least with a rigid model. Dieke[16] has already calculated a specific heat curve with quarter quanta, but this is not as satisfactory as some of the other curves.

Until recently half as well as quarter quanta were often ascribed to the existence of an $\epsilon\neq 0$, for in the absence of a basis for half quanta in the old quantum theory it was commonly supposed that m was integral and that $\epsilon=\frac{1}{2}$. This was done even in bands not susceptible to magnetic fields, regardless of the fact that with an $\epsilon\neq 0$ there should be an observable Zeeman effect (of the order $1/m$ times the normal separation). Fortunately the new quantum mechanics has furnished a natural basis for half quanta (cf. section 1) and thus made unnecessary the assumption $\epsilon=\frac{1}{2}$ in most cases. As noted to the writer by Dr. Mulliken, the facts of band spectra still sometimes demand an $\epsilon\neq 0$, but this effect is probably not due to a rigidly fastened electronic angular momentum of the Kramers-Pauli type, but rather to loose coupling of the spin axis of the electron, which makes this axis orient itself relative to the combined nuclear and orbital angular momentum rather than relative to the orbital alone. We then have coupling of Hund's[33] type (*b*), which

[72] Lucy Mensing, Zeits. f. Physik, **34**, 602 (1926). Miss Mensing also shows that in any case it is impossible to have simultaneously a stationary normal component $\epsilon h/2\pi$ of angular momentum and a component $\sigma h/2\pi$ parallel to the axis of figure. She does not consider explicitly angular momentum due to internal spins of the electrons, but it is not likely that its inclusion will modify the conclusions.

[73] This precession is intimately connected with the existence of doublets in band spectra. See O. Klein, Phys. Rev. **25**, 109A (1925); also Hund, l.c.[33]

gives an expression for the energy in some ways analogous to the Kratzer or Kramers and Pauli formula.

In an important recent paper Curtis and Long[74] have classified a large number of lines in the helium band spectrum with the aid of quarter quanta. The initial states for a given branch are represented either by the series of numbers $\frac{3}{4}, \frac{7}{4}, \cdots$, or else by $\frac{5}{4}, \frac{9}{4}, \cdots$, but not by both series simultaneously. Because of the difficulties mentioned above, it is probable that the quarter quanta should be replaced by half quanta, as suggested by Mecke.[26] This has just been done in Mulliken's significant new analysis[75] of the electronic states and band spectrum of the helium molecule. In each band initial (or final) states are then wanting for every other value of the rotational quantum number, as $\frac{3}{4}, \frac{7}{4}, \cdots$, is replaced by $\frac{3}{2}, \frac{7}{2}, \cdots$, etc. We thus get a limiting case of alternating intensities, in which now every other line is completely missing. Some of the rotational quantum numbers required for the numerical representation of observed spectral terms are not exactly half integers, as ϵ is not always $\frac{1}{4}$ in the Curtis-Long formulae, but the slight deviations are probably due to loose coupling of the spin axes of the electrons relative to the rest of the molecule (cf. Hund[33]).

Owing to centrifugal expansion the rotational energy is not given accurately by the formula (3) based on a rigid model, but instead can be developed as a power series in m^2. The main correction term to Eq. (3) is thus of the form αm^4. It can be shown that theoretically[76] $\alpha = -h^4/128\pi^6 I^3 \nu_0^2$, and hence the nuclear vibration frequency can be deduced from observed values of the coefficient α if the moment of inertia I is known. The value thus obtained for ν_0 is twice as large with quarter as with half quanta since I and m^2 are four times as large with the latter as with the former. Mecke[26] notes that for this reason the use of quarter quanta destroys the regularity in his correlation of vibration frequency with moment of inertia. More specifically, Birge[77] finds that in nitrogen the vibration frequency deduced from α with quarter quanta is twice too large to be reconciled with estimates by other methods. Birge observes that this fact must be regarded as a conclusive argument against quarter quanta.

Zeeman effect. We shall now digress to consider the Zeeman effect

[74] W. E. Curtis and R. G. Long, Proc. Roy. Soc. **108A**, 513 (1925).

[75] R. S. Mulliken, Proc. Nat. Acad. **12**, 158 (1926); also especially Phys. Rev., Dec., 1926.

[76] This is a well-known result in the old quantum theory, and the work of Fues or series expansion of (5) shows that it also holds in the new quantum mechanics.

[77] R. T. Birge, Phys. Rev. **27**, 107 (1926).

of molecules, especially hydrogen, as this subject is of some interest itself and also may throw some light on the structure of excited states.

If there is "rigid coupling" of the spin electrons, the change in energy produced by a magnetic field is

$$-\frac{\mu\sigma n_H}{(m^2-\frac{1}{4})}H \tag{9}$$

where μ is the magnetic moment of the molecule in the direction of the axis of figure, $\sigma h/2\pi$ is the combined spin and orbital electronic angular momentum in this direction, and n_H is the magnetic quantum number, which is proportional to the component of total angular momentum in the direction of the external field. By "rigid coupling" we mean that the spin axes are so firmly bound that their orientations relative to the orbital angular momentum or axis of figure are uninfluenced by the nuclear rotation or by the applied magnetic field. Our formula (9) differs from those given by Kramers and Pauli,[70] Kemble,[78] and others in having $(m^2-\frac{1}{4})$ in place of m^2. That this is the modification required by the new quantum mechanics can be seen from the amplitude matrices for gyroscopic molecules given by Dennison.[7] In Eq. (9) we have, following Hund,[33] included only the contribution of the magnetic moment parallel to the axis of figure, because the normal component will doubtless precess very rapidly about this axis and make only a negligible contribution to the Zeeman separation, unless perchance there is a stationary angular momentum $\epsilon h/2\pi$ normal to the axis of figure. The existence of an $\epsilon\neq 0$ is very unlikely because of dynamical difficulties previously mentioned, but would give rise to a term in the energy proportional to $\epsilon H n_H/(m^2-\frac{1}{4})^{1/2}$ (if[72] $\sigma=0$) and a Zeeman separation of the order $1/m$ instead of $1/m^2$ times the normal separation.

Since by the selection principle m and n_H cannot change by more than one unit, it follows that according to (9) the spacing of Zeeman components should be of the order $1/m^2$ times the normal separation. The number of components should increase and their spacing decrease with increasing values of the rotational quantum number. Actually no Zeeman effect is observed by either Dufour[79] or Croze[80] in the Fulcher bands of hydrogen. This can only mean that the excited states involved in the emission of these bands have no magnetic moment; i.e., are non-gyroscopic. The question, of course arises whether the theoretical separation might be too small to be observable since it is

[78] E. C. Kemble, Phys. Rev. **27**, 799A (1926).
[79] A. Dufour, Ann. de Chim. et Physique **9**, 361 (1906); J. de Physique, **8**, 258 (1909).
[80] F. Croze, Ann. d. Phys. **1**, 63 (1913).

of the order $1/m^2$ times the normal. The experimental error in Croze's experiments, however, is only about 1/50 of the normal separation, and so a magnetic moment could perhaps be detected unless m exceeded about 7, whereas actually m is smaller for most lines observed in the Fulcher bands. Richardson notes[54] that the central line of one of the bands shows traces of a slight effect.

In contrast to the Fulcher bands, certain other lines emitted by the hydrogen molecule have a pronounced Zeeman separation of a quite remarkable type.[79, 80] In such lines the Zeeman pattern sometimes consists of a doublet whose width is approximately (to 25% or so) equal to the distance between the outer components in the normal Lorentz triplet. The two components of the doublet are circularly polarized, but occasionally the sense of the polarization is the reverse of the usual, giving a positive apparent value of e/m. Lines of a similar Zeeman structure have also been observed for a few other molecules, notably BaCl, CaF, etc.[79] As mentioned by Kramers and Pauli,[70] a Zeeman pattern of this character must be due to loose coupling,[81] for we have seen in the preceding paragraph that with rigid coupling there would be more components and smaller separations. Until the advent of the spin electron, it was hard to see how there could be the proper loose coupling, since electron orbits would have to be enormously large compared to the nuclear separation in order to orient themselves freely in magnetic fields, and even then it would be difficult to account for the peculiar type of pattern and polarization. It is now, however, quite certain that the electron has an internal degree of freedom, probably due to spinning, as proposed by Compton[82] and by Uhlenbeck and Goudsmit.[32] Consequently we suggest that the peculiar Zeeman doublets found in molecular spectra are to be attributed to loose coupling of the axes of spin rather than of the orbits themselves, since spectroscopic data shows that the intra-molecular forces which orient the spin axes are much weaker than those which orient the orbit. The loose coupling may be expected only in excited states, for the force orienting the spin axes varies as the inverse cube of the radius of the orbit.[83]

Let us assume the molecule has one valence electron with an orbit so large that its spin axis is negligibly coupled to the molecule and so

[81] J. W. Nicholson has recently discussed the pronounced Zeeman effect in some hydrogen lines and also notes that it indicates a quite different type of structure or coupling than in the Fulcher bands. Monthly Notices, R.A.S. **85**, 449, 656 (1925).

[82] A. H. Compton, J. Frankl. Inst. **192**, 145 (1921).

[83] Cf. L. H. Thomas, Nature **117**, 514 (1926); F. R. Bichowsky and H. C. Urey, Proc. Nat. Acad. **12**, 80 (1926); J. Frenkel, Zeits. f. Physik **37**, 243 (1926).

orients itself freely in a magnetic field. The theory of the anomalous Zeeman effect[84] shows that there are then two possible orientations for the spin axis, viz., parallel or anti-parallel to the field, and that the energy is

$$W = W_0 + 2P_r h\omega_H, \tag{10}$$

where ω_H is the normal Lorentz Zeeman separation, W is the energy in the absence of the field, and $P_r = \pm\frac{1}{2}$ is the axial component of the valence electron's spin angular momentum, measured in multiples of the quantum unit $h/2\pi$. The factor 2 in (10) arises from the doubly large ratio[32] of magnetic moment to angular momentum for internal spins. We have omitted the term contributed by the part of the magnetic moment which is rigidly coupled to the axis of figure and which arises from the orbital motion of the valence electron and from the spin and orbital motions of the other, firmly bound electrons. This neglected term is of the form (9) and hence much less than the contribution $2P_r h\omega_H$ of the spin of the valence electron unless the rotational quantum number m is small.

If there is loose coupling in both the initial and final states, then by (10) the frequency should be approximately the same as without the field, ar else displaced by twice the normal Lorentz value, according as ΔP_r is 0 or ± 1. The unit changes in P_r involve a semi-somersault of the spin axis, and do not appear to be found experimentally, as in atomic spectra a doubly large Zeeman displacement is not found in the Paschen-Back effect, where the spin axis is oriented relative to the applied field. This is probably because radiation is from the orbital rather than spinning motion, and the precession frequency $2\omega_H$ of the spin axis does not appear in the Fourier development of the orbital motions if the coupling between the spin and orbital motion is negligible.[85] It is thus probable that we can only have $\Delta P_r = 0$ and if this is the case there is only a small Zeeman separation of the order ω_H/m^2, even with the loose coupling in both the initial and final states.

To avoid this difficulty the writer wishes to suggest that there is loose coupling in the initial state, but not in the final, or vice versa, so that the term $2P_r h\omega_H = \pm h\omega_H$ in (10) is absent for one of the two states. This hypothesis is attractive, as it gives a Zeeman displacement having the normal Lorentz value ω_H, and with the central undisplaced

[84] We are concerned with the theory for strong rather than weak fields. For summary, cf., for instance, J. H. Van Vleck, l.c.,[36] p. 241. Effects previously attributed to the atom-core are now to be ascribed to internal spins.

[85] This is probably the solution of the difficulty mentioned in note 370 of the writer's Bulletin.[36]

component entirely wanting, as it is experimentally in Dufour's measurements on the fluorides of the alkaline earths. The observed displacements in the doublets are not exactly ω_H and in certain molecules the doublets are resolvable into quartets, but departures from the value ω_H must be expected because there may be a rigidly coupled magnetic moment in addition to the loosely bound spin moment, and also especially because we cannot neglect entirely the coupling between the spin of the valence electron and the remainder of the molecule. A mathematical theory of this interaction will be necessary to ascertain whether the suggestion of a loosely coupled spin in one state will explain the anomalous polarization of some of the lines and the exact quantitative values of the doublet separations. Our suggestion is only tentative. It assumes one loosely coupled electron, and so appears more likely for the bands emitted by the halides of the alkaline earths than for those of molecular hydrogen. The hydrogen molecule contains an even number of electrons, whereas Mulliken[33] ascribes the alkaline earth halide bands to odd, one-valence-electron molecules of the type BaCl, CaF, etc., instead of to the common even structures $BaCl_2$, CaF_2, etc.

If the spin axis is so loosely coupled that it can orient itself freely in an applied magnetic field of ordinary magnitude, it is probable that in the absence of the field its orientation is influenced by the nuclear rotation. We then may have coupling of a type considered by Hund[33] (case b, p. 662 of his article) in which the spin axis is quantized relative to the combined angular momenta of the nuclei and orbit rather than relative to the orbital angular momentum alone. A sufficiently weak field, would not, of course, be adequate to destroy this coupling and the Zeeman separation in such a field has been calculated by Hund.[33] He finds the spacing of components to then be of the order $1/m$ times the normal Lorentz separation or considerably smaller than the distance between the doublet components observed by Croze and Dufour. There must therefore be a sort of Paschen-Back effect whereby the internal coupling is overpowered and the closely spaced components merged into a wide doublet. This transition has apparently not been observed experimentally, but as noted by Hund, may be difficult to detect since the internal coupling may be so weak that it breaks down completely in any field strong enough to give a measurable Zeeman effect.

4. Absolute Entropies and Chemical Constants

The theory of specific heats is intimately related to that of chemical constants, as both must involve the same a priori probability, moment of inertia, etc.

Chemical constant of a thermally monatomic gas. The formula for the entropy of a gram-mol of thermally monatomic gas is

$$S=\tfrac{5}{2}R\ln T-R\ln p+\tfrac{5}{2}R+CR\ln 10, \tag{11}$$

where R is the gas constant and C is the so-called "chemical constant" which appears in the vapor-pressure equation and which determines the absolute value of the entropy. We denote natural and common logarithms throughout by ln and log respectively. By a "thermally monatomic" gas we mean one whose specific heat c_p at constant pressure has the classical equipartition value $\frac{5}{2}R$ for a perfect monatomic gas. Here and elsewhere we neglect the possibility of a "degeneration" of c_p below the value $\frac{5}{2}R$, as this can take place only under extreme conditions (cf. end of Section 2). The theoretical value of C determined from quantum statistics is

$$C=\log[(2\pi m)^{3/2}k^{5/2}/h^3P]+\log p_0-\log\sigma=-1.587+\log(M^{3/2}p_0/\sigma) \tag{12}$$

where m is the mass of a molecule, M is the molecular weight and $P=1.0132\times10^6$ is the value of atmospheric pressure in dynes/cm^2. The factor P^{-1} is included in order that the pressure p in (11) may be expressed in atmospheres. p_0 denotes the a priori probability of the stationary state of lowest energy. In a monatomic molecule (atom) this state is simply the spectroscopic normal state, while in a diatomic molecule it is the state of minimum rotational quantum number, which is occupied by practically all molecules near the absolute zero. σ is the Ehrenfest-Trkal symmetry number, defined as the "number of orientations in space in which the molecule is statistically equivalent", and is not to be confused with the spin quantum number for gyroscopic molecules used in Section 2, which was also denoted by σ. In monatomic molcules we may neglect the term $-\log\sigma$, as here $\sigma=1$. For a "non-polar", symmetrical diatomic molecules such as H_2, the value of σ is 2, while $\sigma=1$ in polar, asymmetric molecules such as HCl.

Our expression (12) for the chemical constant differs from the ordinary Stern-Tetrode[87] formula by the presence of the additional terms $\log p_0$ and $-\log\sigma$. These terms are not usually included, but seem to be demanded with any rational application of quantum statistics. The theoretical necessity of adding the term $\log p_0$ appears to have been first suggested by Shottky[88] and especially R. H. Fowler,[89] and its

[87] H. Tetrode, Ann. der Phys. **38**, 434 (1912); O. Stern, Phys. Zeits. **14**, 629 (1913).

[88] W. Schottky, Phys. Zeits. **22**, 1 (1921); Ann. der Physik, **68**, 481 (1922); also particularly Phys. Zeits. **23**, 9 (1922).

[89] R. H. Fowler, Phil. Mag. **45**, 32 (1923); **1**, 845 (1926).

possible utility in explaining experimental results has recently been stressed by Simon,[90] Eucken and Fried,[91] and others. This term is probably required even in the Einstein-Bose[38] statistics, although it has ordinarily been omitted in the latter. If the temperatures are so low that practically all atoms are in the lowest quantum state, we need consider only the translational degrees of freedom, but the number of cells between two given values of the translational energy is presumably p_0 times that assumed by Einstein (if $\sigma=1$) and the application of the Einstein-Bose theory with this modification yields the extra term $\log p_0$. The Einstein-Bose gas degeneration then does not make the entropy of a monatomic gas vanish at the absolute zero, as ordinarily stated. Instead the degraded value of the entropy becomes $R\ln p_0$ at $T=0$ in the absence of external fields. The Nernst heat theorem would thus not be applicable even to a monatomic gas (where $\sigma=1$) except for the fact that sufficiently near $T=0$ the application of an infinitesimal external field makes practically all the molecules select the one particular orientation of minimum energy, rather than all p_0 orientations, so that the effective a priori probability might then be 1 instead of p_0. The term due to the symmetry number σ is less easily deduced than $\log p_0$, but its necessity can be seen from the statistical work[92] of Ehrenfest and Trkal, Partington, and R. H. Fowler.

In monatomic gases there is as yet no exact quantitative experimental evidence for the additive term $\log p_0$ in (12). For discussion of the data, and references, the reader is referred to a very complete recent paper by Simon.[90] Some of the most satisfactory data confirming the Stern-Tetrode formula is for He, A, and Hg,[93] and here the additive term vanishes since the normal states of these atoms are S-terms with $p_0=1$. This perhaps explains why the Stern-Tetrode formula is so often given and accepted in unmodified form. In the alkalis there are two orientations for the normal state in a magnetic field, so that the additive term has the value $\log 2=.3$. Simon[90] shows that revised

[90] F. Simon, Zeits. f. Phys. Chem. **110**, 572 (1924).

[91] A. Eucken and Fried, Zeits. f. Physik **29**, 36 (1924).

[92] P. Ehrenfest and V. Trkal, Proc. Amsterdam Acad. **23**, 162 (1921); J. R. Partington, Phil. Mag. **44**, 988 (1922); **46**, 329 (1923); R. H. Fowler, *ibid.* **45**, 1 (1923), especially p. 32.

These writers do not express their results in the form (12). Instead they deduce Eq. (15), but (12) is easily derived from (15), as we show after (15).

[93] The values for Hg, however, are rather high, as Simon (Zeits. f. Phys. Chem. **107**, 279, 1923) finds C to be .08 larger than required by theory and Rodebush and Dixon (Phys. Rev. **26**, 851, 1925) find C to be .19 larger. The latter state the discrepancy is within the experimental error but Simon claims an error of only .06.

data of Ladenburg and Minkowski for Na and K and of Scott for Rb and Cs give chemical constants very nearly .3 in excess of the Stern-Tetrode value. On the other hand Rodebush and Devries[94] recently find a constant for Na only .08 in excess, and estimate their experimental error to be but .1. Simon shows that the chemical constants for several other elements, notably Wohl's values for Cl, Br, and I, are .5 or more higher than the Stern-Tetrode values, indicating a $p_0 \neq 1$ in these substances, but the data are scarcely adequate for quantitative inferences concerning the magnitude of p_0.

Chemical constant of hydrogen at low temperatures. Eqs. (11) and (12) can be applied to a diatomic gas only if the temperature is so low that rotational quanta are not excited. This condition is realized experimentally only in hydrogen. Here the most accurate experimental value of C is probably that of Simon,[95] who finds $C = -1.11 \pm .03$, which agrees[96] within the limits of error with the unmodified Stern-Tetrode value $-1.59 + \frac{3}{2} \log 2.016 = -1.13$. This is consistent with (12) only if the terms $\log p_0$ and $-\log \sigma$ cancel. Since $\sigma = 2$ in H_2, such a cancellation would require that the a priori probability of the lowest rotational state be 2, as emphasized by Fowler.[89] Also as the a priori probability is in general $2m$, the whole quantum values 1, 2, $\cdots$ would needs be assigned the rotational quantum number m, yielding a specific heat curve of the type (*a*) discussed in Section 2. Unfortunately we have seen in Sections 1 and 2 that it is doubtful whether such whole quanta are allowable in the new quantum mechanics. It is notable that the Nernst heat theorem applies if we use whole quanta in non-polar molecules and half quanta in polar, as then $p_0 = \sigma = 2$ in the former and $p_0 = \sigma = 1$ in the latter, so that in either case the additive term $\log (p_0/\sigma)$ vanishes but this may well be only a spurious argument for the whole quanta. If in hydrogen we assumed the half quanta $m = \frac{1}{2}, \frac{3}{2}, \cdots$ (case *d*, Section 2) we would have $p_0/\sigma = \frac{1}{2}$ and $C = -1.43$ if the symmetry number σ is retained,[97] while with half-quanta commencing at $m = \frac{3}{2}$ (cases *b* and *c*, Section 2),

[94] W. H. Rodebush and T. Devries, J. Amer. Chem. Soc. **47**, 2493 (1925).

[95] F. Simon, Zeits. f. Physik, **15**, 307 (1923).

[96] Eucken, Karwat, and Fried,[107] on recalculating Simon's data and using somewhat different heats of vaporization find $C = -1.09 \pm .02$ which does not agree with the Stern-Tetrode value -1.13 within their estimate of the experimental error. There has been considerable controversy between these writers and Simon[99] regarding whose value of C is more accurate. In his last paper Simon claims to find a numerical error in Eucken's calculations.[97]

[97] F. Simon, Zeits. f. Physik **33**, 946 (1925).

p_0 becomes 3 and $C=-.95$. Neither of these values for C agrees at all with Simon's.[98]

At this point it must be emphasized that the experimental value $C=-1.11$ is deduced from vapor pressure measurements on the assumption that the Planck extension of the Nernst heat theorem can be applied to the solid phase, so that the entropy of the latter can be taken to be zero at $T=0$. This assumption is, however, scarcely more or less admissible than the unmodified Stern-Tetrode formula for the gaseous phase. Instead, it appears more satisfactory to assume that at $T=0$ the entropy of the solid phase is

$$S=R\ln p_s-R\ln\sigma_s \tag{13}$$

where p_s is the a priori probability associated with the normal state in the solid. The need of the term $R\ln p_s$ was first suggested by Shottky[88] and has also been mentioned by Simon,[90], Eucken and Fried,[91] and others. None of these writers introduce a symmetry number σ_s for the solid phase, but I see no reason why there may not be such a number for solids as well as gases, since solid molecules subject to inter-molecular forces can probably to some extent, at least, be regarded as limiting cases of gas molecules subject to strong external fields. Of course there can be no free rotations in a true solid, but nevertheless there may be degrees of freedom and quantum numbers corresponding to those associated with rotations in a gas.

If we admit (13), the effective chemical constant appearing in the vapor pressure equation is not the constant C appearing in the absolute entropy of the gas according to (11, 12), but instead can be shown to be $C_{eff}=C-\log(p_s/\sigma_s)$. Then according to Simon's data C_{eff}, not C, has the Stern-Tetrode value in hydrogen, and this simply means that the symmetry number and minimum a priori probability have the

[98] On the basis of his theory of ultimate rational units, G. N. Lewis has proposed the value

$$C=\log[k^{5/2}m^{3/2}8\pi^5/15h^3\epsilon^{5/2}P]=-1.66+\log M^{3/2} \tag{12'}$$

for the chemical constant. (See, for instance, Lewis and Randall, Thermodynamics, p. 456. Lewis does not give his result in the form (12'), but (12') is readily deduced from his expression for the absolute entropy and his relation connecting ϵ, h, and c. Cf. Dushman, Phys. Rev. **21**, 623, 1923. We here denote the electronic charge by ϵ, not e, as $e=2.718$ in 12'.) In hydrogen Eq. (12') gives $C=-1.20$ which does not agree with experiment nearly as well as the Stern-Tetrode value -1.13. In getting (12'), Lewis assumes that an undetermined numerical factor has the value unity. He mentions that this factor might possibly be some other "simple number." If his theory is to be reconciled with (12), this number must be $15p_0\epsilon^{5/2}/2^{3/2}\pi^{7/2}\sigma$, which is not particularly simple but is nearly unity if $p_0/\sigma=1$. This coincidence perhaps explains why (12') is often in approximate accord with experiment.

same ratio in the gaseous and solid phases, making C_{ett} equal the first log in (12). Since it is not unlikely that in hydrogen $\sigma=\sigma_s=2$, we can thus have $p_0=1$ (case *d*, Section 2) without contradicting vapor pressure measurements if also $p_s=1$. Similarly the effective chemical constant C_{ett} of sodium might have the unmodified Stern-Tetrode value if there are two equally probable orientations for atoms in the solid state, but this seems unlikely in view of the magnetic moment or polarity of alkali atoms.

We have seen in Section 2, cases *b* and *c*, that there is some evidence for half quanta in hydrogen commencing with the value $\frac{3}{2}$. According to the above, this is consistent with Simon's data if $p_s=3$. It is easy to grant two configurations of equal energy in solid hydrogen, as configurations obtained from each other by rotation through 180° are statistically equivalent owing to non-polarity. It is, however, hard to imagine the three positions of sensibly equal energy which are required if $p_s=3$. Their energies would have to agree to within less than 10^{-3} volt to secure virtually equal probabilities at Simon's lowest measured temperature $T=11°$. Only one or two configurations might be occupied at the absolute zero, and, as noted by Simon,[99] there would then be an unobserved anomaly in the specific heat of the solid between the $T=0$ and $T=11°$, since the specific heat would show a sharp maximum at the temperature of transition from one or two to three configurations. In support of the possibility $p_s=3$, we may cite a very interesting recent paper by Pauling and Tolman,[100] in which several orientations of equal energy are considered possible in a supercooled liquid but not in a crystalline solid, in accord with Lewis and Gibson's[101] observation of larger entropies for the former than the latter. On the other hand the solid hydrogen produced experimentally is probably to some extent crystalline, and Professors Darwin and Fowler inform the writer that for the crystal as a whole the symmetry number is unity. Of course it may be different for a single molecule, but it is uncertain how far individual molecules can be quantized in a crystal. Unit symmetry number in the solid would destroy all agreement with experiment if $p_0=3$ unless the symmetry number is omitted in the gaseous phase. It is, however, not certain how far symmetry numbers should be employed in statistical problems, although in some cases their necessity is unavoidable. We have already in Section 2 seen the difficulties connected with Ehrenfest and Tolman's attempt

[99] F. Simon, Zeits. f. Physik, **31**, 224; **33**, 946 (1925).
[100] L. Pauling and R. C. Tolman, Journ. Amer. Chem. Soc. **47**, 2148 (1925).
[101] Lewis and Gibson, *ibid.* **42**, 1529 (1920).

to introduce the symmetry number into the quantization. At any rate any inferences about the chemical constants of gases made from vapor pressures seem rather uncertain until we have a clearer insight into the exact significance of symmetry numbers or a more complete statistical theory of the a priori probabilities of molecules in solids. On the whole, the most conservative interpretation of the experimental situation in hydrogen is probably simply that the minimum a priori probability is the same in the solid and gaseous phases.

Chemical constant for diatomic gases at high temperatures. If the temperature is high enough so that the rotational, but not the vibrational, degrees of freedom are excited, the specific heat of a perfect diatomic gas is $c_p=\frac{7}{2}R$ and its entropy per gram mol is

$$S=\tfrac{7}{2}R\ln T-R\ln p+\tfrac{7}{2}R+C'R\ln 10. \tag{14}$$

The corresponding chemical constant C is

$$C'=\log[(2\pi m)^{3/2}k^{7/2}8\pi^2 I/h^5 P\sigma]=36.81+\log(M^{3/2}I/\sigma) \tag{15}$$

where I is the moment of inertia. Eq. (15) was obtained independently by various authors, and differs from an early formula of Sackur[102] in the inclusion of the symmetry number. Eqs. (14) and (15) may be obtained in a simple manner from (11) and (12), or vice versa, by noting that the total entropy (14) is the sum of the entropy (11) for a thermally monatomic gas and the rotational entropy

$$S_r=\int_0^T c_r d\ln T. \tag{16}$$

This integral is easily evaluated by a method given by Tolman and Badger.[103] We shall assume a rigid molecule so that the specific heat given by Eq. (1) is all rotational. We substitute in (16) the value (1) for c_r, change the variable of integration from T to $\rho=1/kT$, and integrate by parts. Thus it is easily found that

$$S_r=R(\ln Q-\rho d\ln Q/d\rho)_0^T \tag{17}$$

At the lower limit the expression in parentheses is simply [104] $R\ln p_0$, while at sufficiently high temperatures we may find the value at the

[102] O. Sackur, Ann. der Physik, **40**, 67 (1913).

[103] R. C. Tolman and R. M. Badger, J. Amer. Chem. Soc. **45**, 2277 (1923). A somewhat similar procedure has also been given in papers by Planck, (Verhd. d. D. Phys. Ges. **17**, 418, 1915) and Rotszajn.[21]

[104] The calculation is most simply made by assuming the additive constant in the energy to be so normalized that the energy vanishes at $T=0$. This is legitimate as we have seen in Section 1 that this constant does not affect the rotational specific heat.

upper limit by replacing the summation in (2) by an integral in a well-known way. Under very general assumptions[105] this procedure gives

$$Q(T)=8\pi^2IkT/h^2, \qquad S_r/R=1+\ln(8\pi^2IkT/h^2p_0) \tag{18}$$

from which (14) and (15) readily follow. Special instances of the formula for S_r have been given by Tolman and Badger and others.

Chemical constant of hydrogen at high temperatures. Vapor pressure measurements cannot be employed to test directly the validity of Eq. (15) for hydrogen, as rotational quanta are adequately excited only far above its critical point. The value of

$$C'-C=(S_r-R-R\ln T)/R\ln 10$$

can be calculated from observed specific heat data by graphical evaluation of the integral in (16) with Eucken's values of c_r. This has been done by Eastman[106] and by Eucken, Karwat, and Fried,[107] who thus find $C'-C=-2.60$. On the other hand the theoretical value of $C'-C$ is

$$C'-C=\log(8\pi^2Ik/h^2p_0)=38.40+\log(I/p_0), \tag{19}$$

as is seen on subtracting (12) from (15). Substitution of the value $C'-C=-2.60$ in (19) gives $I=1.0p_0\times10^{-41}$ gm. cm.^{2} Unfortunately in comparing theoretical and experimental values of $C'-C$, Eucken, Karwat, and Fried use the Sackur formula[102] for C' and the unmodified Stern-Tetrode formula for C. They thus get $I=1.0\times10^{-41}$. This value of I is quoted by Schrödinger[27] in support of his type of specific heat formula (*d*, Section 2) which yields a lower moment of inertia 1.4×10^{-41} than most of the other theoretical specific heat curves. The value $I=1.0\times10^{-41}$ appears to me clearly erroneous because the factor p_0 is omitted. The theoretical calculation of C or C' involves some rather abstruse statistical questions, but the determination of $C'-C$ is relatively simple for it involves only the evaluation of (17) with Q defined by (2). The result is (19) regardless of whether whole or half quanta are used, provided only the molecule be considered rigid. Lessheim[17] suggests that there is an uncertainty log 2 in the theoretical

[105] The asymptotic formula (18) for $Q(T)$ is valid equally well with whole or half quanta and either with or without exclusion of the state $m=0$ or $m=\frac{1}{2}$. It holds with any a priori probability of the form $2m+a$, where a is any number independent of the rotational quantum number m. In the new quantum mechanics a is zero at least in polar molecules such as HCl, but the value of a is immaterial as regards $Q(T)$ since it gives[108] only a term proportional to $T^{1/2}$ which can be omitted. If every other state is excluded (case *c*, Section 2) our formulas, however, must be modified, as a term $-R\ln 2$ must then be added to S_r and $-\log 2$ to C'.

[106] Eastman, J. Amer. Chem. Soc. **44**, 1008 (1922).

[107] Eucken, Karwat, and Fried, Zeits. f. Physik, **29**, 1 (1924); **32**, 150 (1925).

formula for $C'-C$, but with this I cannot agree, as Eq. (19) is based only on simple specific heat theory and so the question of a symmetry number, etc., cannot enter. The comparison of theoretical and experimental values of $C'-C$ in hydrogen consequently does not furnish any new criterion for determining the moment of intertia other than that already found in specific heats.[108] With whole quanta the minimum a priori probability is 2 and then the moment of interia deduced from $C'-C$ is 2.0×10^{-41} gm. cm^2 (not 1.0×10^{-41} as usually stated), which agrees closely with Reiche's value 2.10×10^{-41} or Kemble and Van Vleck's value 1.98×10^{-41} deduced from a specific heat curve of type (a), Section 2. With the half quanta $m=\frac{3}{2}, \frac{5}{2}, \cdots$ (case b, Section 2), we have $p_0=3$ and Eucken's value of $C'-C$ then gives $I=3.0\times10^{-41}$, while Hutchisson finds that $I=2.99\times10^{-41}$ gives the best specific heat curve of type (b). The agreement of the two methods of estimating I is not a particularly crucial test, as the ability to give the proper value of $C'-C$ and hence the integral in (16), i. e., the proper area under a curve, is not nearly as exacting a test as the representation of the specific heat curve itself.

In distinction from the above considerations, accurate measurements of the dissociation equilibrium of hydrogen would furnish an independent method of determining C' and hence the moment of intertia. Existing dissociation data does not appear adequate to warrant any definite conclusions, although Simon[90] has discussed some of Wohl's explosion experiments in a preliminary way.

Chemical constants of other diatomic gases. Except for hydrogen, the specific heat of a diatomic gas is generally $\frac{7}{2}R$, or more, even below the critical point, and Eq. (15) can then be tested directly by vapor pressure measurements in cases where the vibrational specific heat is negligible. Comparisons of the theoretical values of the chemical constant or of absolute entropies with experiment have recently been given for several gases by Urey,[108] by Tolman and Badger,[103] by Cox,[109] and by Eucken, Karwat, and Fried,[107] all using in the theory the moments of intertia deduced from band spectra. The paper by Eucken and colleagues in particular surveys the experimental data very carefully. We shall not discuss the numerical results, for they do not yield any definite conclusions, except that Eq. (15) does not hold if solid phases are assumed to have zero entropies at $T=0$. As emphasized by Cox, the one case of really satisfactory agreement is that of nitrogen. Eucken and colleagues conclude that the best experimental value

[108] This is also noted by Urey, J. Amer. Chem. Soc. **45**, 1445 (1923).

[109] R. R. S. Cox, Proc. Cambr. Phil. Soc. **21**, 541 (1923); **22**, 491 (1923).

of C' for nitrogen is $-.11\pm.05$, while Cox, on making an independent calculation from Eucken's data concludes that experimentally $C'=-.15$. Assuming that nitrogen has the moment of inertia 14.2×10^{-40} deduced from band spectra, the theoretical value of C' given by (15) is $-.16$. Omission of the symmetry number $\sigma=2$ would entirely destroy this excellent agreement.

It may perhaps be well to call attention to minor revisions in the calculations of the various authors which are necessary if we accept the statistical theory of Ehrenfest and Trkal, Partington, and R. H. Fowler, all[92] of whom agree on the value (15) for the chemical constant.

Urey, also Badger and Tolman assume that at very low temperatures the chemical constants of diatomic gases conform to a formula[93] of Lewis which is nearly the same as the unmodified Stern-Tetrode formula, instead of to (12). The main revision for their calculated entropies is thus the addition of the term $R\ln(p_0/\sigma)$. From this it can be shown that Urey's entropies S_{298}, also those calculated by Tolman and Badger for their cases V and VI must be increased by $R\ln 2+.3=1.7$ for polar molecules but by only .3 for non-polar molecules. Here the term .3 is merely the difference between the Lewis and Stern-Tetrode absolute entropies. Tolman and Badger endeavor to draw conclusions concerning the form of the a priori probability p_m in (2) from a study of chemical constants at temperatures at which rotations are fully excited. According to the statistical theory of Ehrenfest, etc., this cannot be done, as p_0 does not enter in Eq. (15). If their calculations for their cases I and III are given the proper corrections, the numerical results are the same as for their cases V and VI, modified as above. Cases II and IV are probably untenable.

Eucken, Karwat, and Fried use the Sackur formula for C' in which the symmetry number is absent, although they mention the possibility that such a number should be included. Consequently according to Ehrenfest, etc., the logarithms of moments of inertia calculated from chemical constants on p. 34 of their paper should be increased by $\log 2=.3$ for non-polar molecules. This is indicated in their discussion, where it is noted that the symmetry number does not in general improve the agreement with experiment.

Cox's treatment is based on Fowler's statistical theory, and so contains a full allowance for symmetry numbers, etc.

A difficulty perhaps even more serious than the conflict between moments of inertia deduced from chemical constants and those deduced from band spectra is the fact that chemical constants calculated from vapor pressure measurements do not agree with those calculated from dissociation equilibrium. This has been particularly emphasized in a recent paper by Eucken and Fried,[91] as well as in the article by Cox. To avoid this disagreement Eucken and Fried suggest that the Nernst heat theorem is not of universal validity and that at $T=0$ the entropy of a solid may equal $R\ln p_s$ instead of zero (cf. Eq. (13)). Here, as previously, p_s denotes the a priori probability of the normal state in the solid phase. The experimental values of the chemical constants C' or C for the corresponding gaseous phases are then to be increased by $\log p_s$ in order to leave unaltered the effective chemical

constant appearing in the vapor pressure equation. We have already briefly discussed on p. 1014 the possible theoretical justification for such a procedure. Eucken and Fried find that most of the discrepancy between vapor pressure and dissociation measurements can be removed by assuming that $p_s=2$ for H_2, N_2, I_2, NO, CO, CH_4, but that $p_s=1$ for O_2, HCl, HBr, HI, CO_2, H_2O, NH_3. They also indicate one or two other possible schemes. These empirical values for p_s yet await an adequate theoretical justification, as there is no obvious reason why some of the gases belong to the category $p_s=2$ and others to $p_s=1$. Also Eucken and Fried's conclusions have been questioned by Simon[99] on the ground that the experimental evidence is inadequate. We may, however, note that most of the gases for which they suggest $p_s=2$ are of a non-polar character, and this may possibly have something to do with the fact repeatedly emphasized in Section 2 that the simple rotator theory used in HCl, etc., cannot be applied to non-polar molecules. We have seen that there is some evidence that in such molecules the minimum value of the rotational quantum number is $\frac{3}{2}$ instead of $\frac{1}{2}$, and this might imply a larger value of p_s, possibly $p_s=3$. Also Pauling and Tolman[100] have noted that in supercooled liquids there may be several configurations of sensibly equal energy, giving a large p_s, and we may add that more configurations might perhaps be expected with non-polar molecules because the orientation has less influence on the energy. If a symmetry number $\sigma_s=2$ is introduced for non-polar molecules in the solid phase, the larger a priori probability would in part be offset by the term $-R\ln 2$ (cf. Eq. 13) and we would then require $p_s=4$ instead of $p_s=2$ to make $S_0=R\ln 2$ for H_2, N_2, etc. as in Eucken and Fried's scheme given above. According to this scheme we would have for hydrogen gas $C=-1.11+\log 2=-.81$. This can be reconciled with Eq. (12) only if the minimum a priori probability p_0 for the gas is 4, or if the symmetry number σ is omitted. The value $p_0=4$ is scarcely conceivable (much less so than $p_s=4$) and the omission of the symmetry number in the gas is questionable since the statistical theory for this number is much more firmly founded in gases than solids. We have seen in Section 2 that there is some evidence for $p_0=3$, but this would increase C by $\log\frac{3}{2}=.18$ instead of by .3 as proposed by Eucken and Fried. Their increased value of C' for nitrogen is consistent with (15) only if the symmetry number σ is omitted or if the moment of inertia be given an unlikely value considerably greater than that obtained from band spectra, whereas we have seen that without Eucken and Fried's modification there was excellent agreement

in this particular case. In short the correlation of experimental and theoretical chemical constants is at present in a decidedly chaotic state.

The writer wishes to thank Professors Bohr, Darwin, and R. H. Fowler, and also Dr. G. Breit, for the opportunity of discussing with them certain parts of this paper.

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August, 1926.

ON THE QUANTUM THEORY OF THE SPECIFIC HEAT OF HYDROGEN

PART II

COMPARISON OF VARIOUS THEORIES WITH EXPERIMENT

By Elmer Hutchisson

Abstract

The most recent experimental data on the specific heat of hydrogen are reviewed and average values are given for various temperatures up to 1000°K. At room temperatures many values are available but they do not check among themselves. At high temperatures the values of the specific heat are not at all certain. Computations are made using different minimum values of the rotational quantum numbers and different a priori probabilities for both rigid and elastic models. The most successful temperature specific heat curve at both high and low temperatures and based upon an elastic model is obtained with (*a*) the a priori probability $p=2m$ for whole quanta and (*b*) $p=2m$, $m=\frac{1}{2}$ excluded, for half quanta. It is shown that half integral vibrational quantum numbers do not appreciably affect the specific heat except to change an arbitrary constant. In scheme (*b*) the normal vibration frequency agrees almost exactly with the value which Witmer has obtained from spectroscopic measurements.

Introduction

THE decrease of the specific heat of hydrogen below the classical value for a diatomic gas at low temperatures was first predicted by Nernst[1] in 1911 and was observed by Eucken[2] in 1912. In the last few years many theories have been advanced to explain this variation. It is the purpose of Part II to examine critically these theories by means of computations based mostly upon the theory discussed by J. H. Van Vleck in Part I. Comparison with experiment is made considering especially the experimental data recently published on the temperature variation of the specific heat of hydrogen.

Experimental Data

Experimental data on the specific heat of hydrogen are available over wide ranges of temperature. Keesom and Kamerlingh Onnes[3] have determined the atomic heats from 11.2°K (below the freezing

[1] W. Nernst, Berl. Ber. p. 65 (1911).

[2] A. Eucken, Sitz. d. Kon. Preus Akad. d. Wis. **1**, 141 (1912).

[3] Keesom and Kamerlingh Onnes, Konink. Akad. Weten. Amsterdam, **18**, 1247 (1916); **20**, 1000 (1918).

point of hydrogen) to 20.11°K. Eucken[3] gives the value for the molecular heat C_v at temperatures ranging from 35°K, where it is $\frac{3}{2}R$ to 273°K, where the value reaches approximately $\frac{5}{2}R$. His values have been criticized because he used a steel container whose specific heat was very uncertain at low temperatures. However, at these low temperatures the heat capacity of the containing vessel is small and his results have been checked very recently and still furnish valuable points on the temperature specific heat curve.

At room temperatures, the work of many observers is available, but the disagreement between them is in some cases just enough to favor one theory rather than another. At 290°K, we find the values of the rotational specific heat ($C_r = C_v - \frac{3}{2}R$) vary from approximately 1.83 to 1.90 cal/mol/degree and the values at both extremes have been checked by more than one observer. The most recent work is that of Partington and Howe[4] and if we may consider their objections to Binkworth's[5] experiments valid (i. e., in the application of a correction factor), then the evidence is almost overwhelmingly in favor of the lower values since they are supported by the experiments of Trautz and Hebble,[6] Trautz and Grosskinsky,[7] and Gruneisen and Merkel.[8] Considering also the values of Giacomini[9] a fair average is approximately 1.85 cal/mol/degree at 290°K.

It has always been impossible to find reliable specific heat curves which would pass through Eucken's value of 1.41 cal/mol/degree at 196°.5K. which was checked almost exactly by Scheel and Heuse.[10] With the appearance of Brinkworth's value of approximately 1.51 the chance appeared that the early values might be in error. But immediately Giacomini published his results which provided a decided check for the first values and if the objections of Partington and Howe are sustained, Brinkworth's value must be lowered. The difficulty therefore still exists that there is a real discrepancy between experiment and theory in the slope of the specific heat curves between 120° and 220°K.

The experimental values at high temperatures are due mainly to one observer. Pier[11] obtained average values for the specific heat from

[4] J. R. Partington and A. B. Howe, Proc. Roy. Soc. **109**, 286 (1925).
[5] J. H. Brinkworth, Proc. Roy. Soc. **107**, 510 (1925).
[6] M. Trautz and K. Hebble, Ann. der Phys. **74**, 285 (1924).
[7] M. Trautz and O. Grosskinsky, Ann. der Phys. **67**, 462 (1922).
[8] E. Gruneisen and E. Merkel, Ann. der Phys. **66**, 344 (1921).
[9] F. A. Giacomini, Phil. Mag. **49**, 146 (1925).
[10] K. Scheel and W. Heuse, Ann. der Phys. **42**, 473 (1913).
[11] M. Pier, Zeits. f. Elektrochemie **15**, 356 (1909); **16**, 897 (1910).

17°C to as high as 2350°C. In his experiments he used the explosion method. By combining the values of Scheel and Heuse at room temperatures with Pier's data, Kemble and Van Vleck[12] have deduced an empirical curve which fits Pier's data better than his own linear relation. Bjerrum[13] and later Siegel[14] have applied corrections to Pier's values for heat loss and for dissociation. According to Partington and Schilling,[15] these corrections should be applied to the original Pier relation. No instantaneous values are available at high temperatures so that on the whole we must conclude that the results at high temperatures are not at all certain. Crofts[16] has also made observations at high temperatures but his results do not fit the curves obtained from other data. Average experimental values for various temperatures are given in Table II.

Theoretical Development

In order to explain theoretically the decrease in the specific heat of hydrogen the quantum theory is used. The essential points in the investigations of the later workers are given in Table I.

Table I

Investigator	Model Assumed	Quanta	A priori probability
Reiche[17] (Curve V)	Non-gyroscopic, Rigid	Whole	$p=2m, \quad m\neq 0$
Kemble and Van Vleck[12]	Non-gyroscopic, Elastic	Whole	$p=2m, \quad m\neq 0$
Tolman[18]	Non-gyroscopic, Rigid	Half	$p=2m+1, \; m\neq 0$
Schrödinger[19]	Non-gyroscopic, Rigid	Half	1:2:4 and 4:7:17

The pioneer work, prior to 1919, was well summarized by Reiche[20] and is therefore not listed in the table. Reiche showed that the temperature-specific heat curve may assume many shapes depending upon the choice of the a priori probability of the various quantum states. Some of these curves give the correct qualitative shape but do not give the correct values at room temperatures, when made to agree with experiment at low temperatures. To obtain values which check better at room temperatures and which account for the abnormal high values of the specific heat (above the classical value $C_v=\frac{5}{2}R$) at high temperatures it is necessary to consider not only the rotational energy of the molecules but also the vibrational energy and the in-

[12] E. C. Kemble and J. H. Van Vleck, Phys. Rev. **21**, 653 (1923).
[13] N. Bjerrum, Zeits. f. Elektrochemie **17**, 731 (1911); **18**, 101 (1912).
[14] W. Siegel, Zeits. f. Phys. Chemie, **87**, 641 (1914).
[15] J. R. Partington and W. G. Schilling, *The Specific Heat of Gases*, London (1924).
[16] J. M. Crofts, J. Chem. Soc. **107**, 290 (1915).
[17] F. Reiche, Ann. der Phys. **58**, 657 (1919).
[18] R. C. Tolman, Phys. Rev. **22**, 470 (1923).
[19] E. Schrödinger, Zeits. f. Physik. **30**, 341 (1924).
[20] F. Reiche, The Quantum Theory, Chap. V, Section I.

crease of energy which is caused by the expansion of the molecules due to centrifugal force. Kemble and Van Vleck[12] have developed a theory containing these factors which agrees fairly well at both room temperatures and at high temperatures with the available specific heat data. In their work they assume a non-gyroscopic model neglecting the electronic angular momentum, and using only whole quantum numbers. Their values are listed in a row (a) of Table II.

In a recent paper Lessheim[21] has taken into consideration the electron angular momentum parallel and perpendicular to the figure axis for a rigid molecule and he has compared the results obtained by using various values of the a priori probabilities and various values of the electron angular momentum. In Part I of this paper, Van Vleck obtains expressions for the specific heat according to the new quantum dynamics. An expression for the energy of an elastic gyroscopic molecule is also incidently given. The rotational and vibrational specific heat is

$$C_r=\frac{N}{J'}\frac{d}{dT}\frac{\sum_n \sum_m p^n_m W^n_m e^{-W^n_m/kT}}{\sum_n \sum_m p^n_m e^{-W^n_m/kT}} \tag{1}$$

where p^n_m is the a priori probability of the mth rotational state and the nth vibrational state, J' is the mechanical equivalent of heat and N is Avogadro's number. An electronic angular momentum $\sigma h/2\pi$ parallel to the axis of figure and $\epsilon h/2\pi$ perpendicular to the axis is assumed. The energy W^n_m of an (m, n) state is given by

$$W^n_m=\frac{h\nu_1}{2}\left(\frac{\nu_0}{\nu_1}\right)^2\left[1-\frac{1}{\left\{(\nu_1/\nu_0)n+\sqrt{1+(\nu_1/\nu_0)^2\left[\sqrt{m^2-\sigma^2}-\epsilon\right]^2}\right\}^2}\right] \tag{2}$$

where ν_1/ν_0 is the ratio of the rotational to the vibrational frequency. The rotational frequency is a function of the moment of inertia, J, so that J and ν_1/ν_0 may be considered as adjustable constants to bring the curve into agreement with experiment at two given points.

Computations

By giving σ, ϵ and m different values in the formula (1) for C_r many different temperature specific heat curves may be obtained. Computations were made with several of these to see if satisfactory values of σ, ϵ and m could be obtained empirically. These different computations are given in Table II together with the results of other investiga-

[21] H. Lessheim, Zeits. f. Physik. 35, 831 (1926).

tors for comparison. The first row give average experimental values. The second gives points on the original Planck curve based upon the simple dipole theory. which goes to a maximum at low temperatures

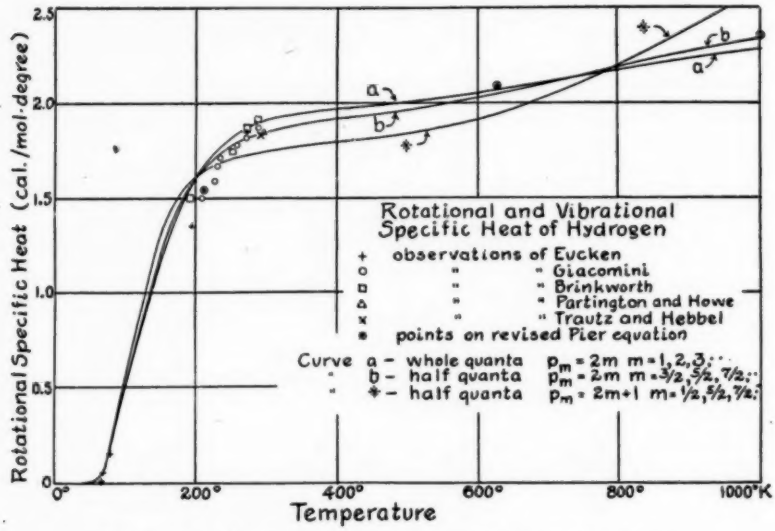

Fig. 1. Rotational and vibrational specific heat of hydrogen.

and therefore cannot agree with experiment. The next row gives points on the curve cited in (*a*) of Section 2 of Part I. Thus curve is that given by Kemble and Van Vleck and is based upon whole quanta. The agreement with experiment is fairly good although according to the present experimental data it is a little high at room temperatures. The second method of removing the specific heat dilemma mentioned in Part I, Section 2, is by use of curve (*b*). In this computation the state $m=1/2$ is arbitrarily excluded. This curve agrees with experiment about as well as curve (*a*); it goes lower at room temperatures but higher at high temperatures. For this curve J has the value 2.989×10^{-41} gm cm and ν_1/ν_0 has the value 0.0424 giving as the normal vibration frequency $\nu_0=1.31\times10^{14}$ sec.$^{-1}$. These calculations were first reported in December, 1924.[22] Later Dieke[23] working independently, also found that excluding the state $m=1/2$ gave good agreement at low temperatures using a rigid molecule. Curves (*a*) and (*b*) are compared in Fig. (1) showing their agreement with available experimental data up to 1000°K. The fact that Takahashi and also Dieke exclude the initial state $m=1/2$ in their interpretations of

[22] E. Hutchisson and J. H. Van Vleck, Phys. Rev. **25**, 243A (1925).
[23] G. H. Dieke, Physica **5**, 412 (1925).

band spectra has already been discussed by Van Vleck in Part I, Section 3.

TABLE II

Computations on the specific heat of hydrogen

No.	Method	p_m	Min.	J×10^{41}	100°	290°	333°	625°	1000°K
1	Experiment	.....	...	.....	.44	1.85	1.94	2.10	2.36
2	Planck	$2m$	1/2	1.27	.448	2.110	.....	.....	....
a	Kemble and Van Vleck	$2m$	1	1.975	.404	1.899	1.948	2.07	2.28
b	Elastic model	$2m$	3/2	2.989	.48	1.840	1.874	2.04	2.32
5	Reiche, Curve I	$2m+1$	0	0.633	.48	.....	sharp	max.	....
6	Reiche, Curve III	$2m+1$	1	2.214	.44	1.65	.....	....	....
7	Tolmann	$2m+1$	1/2	1.387	.481	1.68	1.69	....	....
8	Elastic Model	$2m+1$	1/2	1.405	.480	1.75	1.769	1.963	2.60
9	Rigid Model	$2m+1$	3/2	3.07	.43	.....	1.709	.....	....
10	Reiche Curve V	$2m$	1	2.095	.44	1.87	.....	.....	...
11	Rigid Model	$2m$	3/2	2.84	.40	.....	1.83	.....	....
12	Rigid Model	$2m-1$	3/2	2.84	.42	.....	2.07	.....	....
13	Schroedinger	1:2:4	1/2	1.43	.44	1.82	.....	.....	....
14	Schroedinger	4:7:17	1/2	1.48	.44	1.80	.....	.....	....

The values listed under Min. are the minimum values of m and thus indicate in each case whether half or whole quanta are to be used and what values are excluded. The a priori probabilities, p_m, are given for the assumption of real half quanta ($\epsilon=0$, $\sigma=0$). For apparent half quanta ($\epsilon=\frac{1}{2}$, $\sigma=0$) the values of p_m are lowered by unity. Some of the values of other investigators have been extrapolated to reduce them to the given temperatures. Other values of ϵ have been considered by Lessheim.[21]

In these calculations the moment of inertia and the ratio ν_1/ν_0 of the rotational to the vibrational frequency were considered as unknowns and adjusted to bring the theoretical curve into as good agreement with experiment as possible. The moment of inertia is virtually assigned by the values at low temperatures, while ν_1/ν_0 is determined a higher temperatures where the vibrational energy comes into play. Most of the theoretical curves fall low at room temperatures when a rigid molecule is assumed. The values may be somewhat raised by using a large value of the ratio ν_1/ν_0 but then the curve will very likely go too high at high temperatures. This is well illustrated in curve (8). An effort was made to make Tolman's assumptions ($p_m=2m+1$ with half quanta) fit experiment using an elastic model. It is seen from Fig. 1 that with these assumptions agreement cannot be had at both low temperatures and high temperatures. In this curve, J has the value 1.405×10^{-41} gm cm and ν_1/ν_0 has the value 0.10.

In the preceding cases ϵ and σ have been taken as zero. Although other values are improbable (see Part I), they are considered to make the table complete. If the minimum value of m is unchanged and $\epsilon=0$ the value of σ does not appreciably affect the specific heat. When $\epsilon=1/2$, values of σ other than zero merely tend to lower the specific heat at room temperatures where it is already too low. To obtain values for which $\epsilon=\frac{1}{2}$ the values of p_m are lowered by unity. Lessheim[21]

also considers the effect of the variation of these quantities. In all of these calculations only those values of the a priori probability are considered which have some theoretical foundation, e. g. $p_m=2m+1$, $2m$, $2m-1$. It will be noticed that curve (12), in which $p_m=2m-1$ and therefore automatically excludes the state $m=\frac{1}{2}$, rises above the classical value at 333° and therefore does not correspond with experiment. Another method of procedure is to consider the a priori probability as unknown and adjust it until the curve fits experiment. This is essentially what is done by Schroedinger.[19] He finds that fairly good agreement may be obtained with the ratio of the successive probabilities 1 : 2 : 4, and using larger numbers, he finds a little better agreement with 4 : 7 : 17. There is, however, no theoretical justification for these values, and they give no clue as to the succeeding probabilities to be used at higher temperatures where more than three quantum states must be considered (see also Part I, Section 2, (*c*) and (*d*)).

Van Vleck notes in Part I that the new matrix dynamics requires half quantum numbers for the vibrational quantum numbers as well as for the rotational quantum numbers. The introduction of vibrational half quantum numbers does not materially change the above results. If we let the ratio of the rotational to the vibrational frequency ν_1/ν_0 be equal to β then the expression for the energy W^n_m given by Eq. (2) becomes, after expansion of the term in the denominator,

$$W^n_m=\frac{h\nu_1}{2\beta^2}-\frac{h\nu_1}{2}\,\frac{1}{n^2+\dfrac{1}{\beta^2}+m^2+2n\sqrt{1/\beta^2+m^2}}\,. \tag{3}$$

Since the ratio β is small compared with the quantum numbers, we can neglect the terms in β upon the expansion of the radical in the denominator. This approximation is justified since it holds to about the same degree of accuracy as the law of force is known. We may then write

$$W^n_m=\frac{h\nu_1}{2\beta^2}-\frac{h\nu_1}{2}\,\frac{1}{(n+1/\beta)^2+m^2}\,. \tag{4}$$

If the whole quantum numbers n be changed to half quantum numbers $n+\frac{1}{2}$ the second term may be brought back to exactly the same form, provided only that we change $1/\beta$ to $1/\beta-\frac{1}{2}$. The change then occurring in the first term has no effect since it remains constant during the summation and drops out. Since in these computations β is considered an unknown constant, it is apparent that the vibrational

half quantum numbers produce no appreciable change in the specific heat. The new quantum dynamics seem to require an a priori probability of $p_m = 2m$. This will give the Planck curve that rises to a maximum near room temperatures and is listed in row 2 of Table II.

Recently, from spectroscopic measurements, Witmer[24] has shown the normal nuclear vibrational frequency to be 1.277×10^{14} sec.$^{-1}$. In the curves (a) and (b), the normal nuclear vibrational frequencies ν_0 are 1.46×10^{14} and 1.31×10^{14} sec.$^{-1}$ respectively. These values were taken to give the best possible agreement with experiment under the assumed conditions. With half integral vibrational quantum numbers required by the new dynamics, these values will be slightly lowered as may be seen from Eq. (4). Curve (b) then gives as the normal vibrational frequency 1.28×10^{14} sec.$^{-1}$ which is in almost exact agreement with Witmer's value. Curve (a) has been roughly recomputed using half vibrational quantum numbers with Witmer's spectroscopic frequency. Agreement with experiment may be obtained at low temperatures but at high temperatures the curve will go higher than the present experimental points. The lack of agreement in curve (a) may be accounted for when we consider that the experimental data at high temperatures is not entirely reliable and since the restoring force is of the form $F(r) = a(r - r_0)/r^3$ (cf. Eq. (4) of Part I) only to a first approximation. In fact, Witmer's data seem to show that actually the departure from non-linearity is much smaller than that for a force of the above type.

The writer wishes to express his sincerest thanks to Professor J. H. Van Vleck for his interest and help throughout these computations.

DEPARTMENT OF PHYSICS,
UNIVERSITY OF MINNESOTA,
September 3, 1926.

[24] E. E. Witmer, Proc. Nat. Acad. Sci. **12**, 238 (1926).

THE SCATTERING OF LIGHT BY GASEOUS MIXTURES AT HIGH PRESSURES

By L. A. Ramdas

Abstract

The intensity of light transversely scattered by pure oxygen, carbon-dioxide and their mixtures in various proportions for pressures ranging from 20 to 120 atmospheres at 32°C, has been measured in terms of the scattering by liquid ethyl alcohol. Some polarization measurements have also been made for pure oxygen and unsaturated carbon-dioxide. The intensity for pure oxygen is proportional to the pressure, whereas for mixtures of increasing percentage of carbon-dioxide, the intensity-pressure curves tend to become more and more similar to the curve for pure carbon-dioxide for which the intensity increases much more rapidly than the pressure. At pressures greater than a few atmospheres, the intensity of scattering ceases to be a linear function of the percentage volume of CO_2 in the mixture.

Experimental Arrangements

RAMAN and Ramanathan[1] found that the intensity of light scattered by carbon-dioxide at high pressures, at which the gas does not obey Boyle's law, is larger than in proportion to the density as indicated by the Einstein-Smoluchowski formula. D. Banerji[2] studied the scattering of light by mixtures of air and carbon-dioxide at atmospheric pressure, and found the intensity of the scattering to vary linearly with the percentage volume of CO_2. The present author undertook to study the effects exhibited by a mixture at higher pressures when it ceases to behave as a perfect gas. The high pressure apparatus used by Raman and Ramanathan in their work with CO_2 was also used for the present investigation. In Fig. 1, A and B are two cylindrical holes, with conical ends, bored in two perpendicular directions into a thick iron cylinder. The ends A and B are fitted with two conical glass windows nicely ground in. The end C is tightly plugged by a steel screw while D is the part fitted with a pin-valve and fitting for connection to the high-pressure reservoirs.

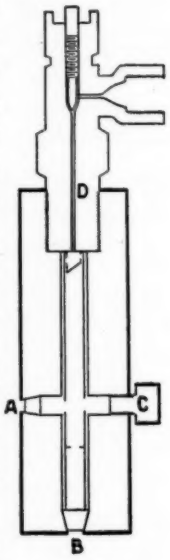

Fig. 1. Diagram of apparatus.

For pure oxygen and carbon-dioxide the commercial steel cylinders filled with the gases at 120 and 75 atmospheres respectively were used as the sources of

[1] C. V. Raman and K.R. Ramanathan, Proc. Roy. Soc. **104A**, 357 (1923).
[2] D. Banerji, Phys. Rev. **26**, 495 (1925).

supply. A mixture of the two gases was prepared by filling a 20 cu. ft. steel cylinder with CO_2 at a pressure of 60 atmospheres at a temperature of 33°C and then connecting it to a cylinder of pure oxygen till the pressure rose to 83 atmospheres. The cylinder now contained both the Einstein-Smoluchowski formula. D. Banerji[2] studied the scattering of light by mixtures of air and carbon-dioxide at atmospheric pressure, and found the intensity of the scattering to vary linearly with the percentage volume of CO_2. The present author undertook to study the effects exhibited by a mixture at higher pressures when it ceases to behave as a perfect gas. The high pressure apparatus used by Raman and Ramanathan in their work with CO_2 was also used for the present investigation. In Fig. 1, *A* and *B* are two cylindrical holes, with conical ends, bored in two perpendicular directions into a thick iron cylinder. The ends *A* and *B* are fitted with two conical glass windows nicely ground in. The end *C* is tightly plugged by a steel screw while *D* is the part fitted with a pin-valve and fitting for connection to the high-pressure reservoirs.

For pure oxygen and carbon-dioxide the commercial steel cylinders filled with the gases at 120 and 75 atmospheres respectively were used as the sources of supply. A mixture of the two gases was prepared by filling a 20 cu. ft. steel cylinder with CO_2 at a pressure of 60 atmospheres at a temperature of 33°C and then connecting it to a cylinder of pure oxygen till the pressure rose to 83 atmospheres. The cylinder now contained both oxygen and carbon-dioxide but apparently not thoroughly mixed together as supplies drawn off from time to time into the observation tube proved to be, at first, nearly pure oxygen, and later, progressively richer and richer in carbon-dioxide. This proved very convenient in practice for studying the scattering in mixtures of varying composition.

The observation tube was flushed with gas and evacuated several times so as to get rid of dust particles. On sending a condensed beam of sunlight through *A*, a blue track could be seen transversely through *B*.

To measure the intensity of the transversely scattered light at different pressures a secondary standard for comparison was used. This was a glass bulb full of pure, dust-free ethyl alcohol. The bulb was blackened completely leaving two small apertures for the light to get through and another for observing the track and fixed above the observation tube. Two narrow, horizontal beams of sunlight, condensed by two good camera lenses provided with adjustable apertures, were passed through the comparison bulb and the observation tube respectively. After cutting off all stray light, a large black screen, provided with two rectangular apertures one above the other, was fixed in front so as to enable the

observer to see only the two blue tracks. The intensities of these tracks could be equalized by adjusting one or the other of the two apertures belonging to the lenses. The readings of the apertures could be easily taken, so that, knowing their equivalent aperture values, the intensity of the scattering by the gas at high pressure in terms of ethyl alcohol could be easily calculated. After measurement of the light scattering, the mixture was allowed to escape from the observation tube and chemically analyzed to find the percentage of CO_2 at 32°C and 1 atmosphere.

Experimental Results and Conclusion

The intensity measurements for pure oxygen, CO_2 and their mixtures in various proportions are given in Table I, in terms of ethyl alcohol.

Table I

Intensity in terms of the scattering of ethyl alcohol

Pressure	100% CO_2	76.4% CO_2	72.45% CO_2	56.4% CO_2	33.3% CO_2	3.6% CO_2	Pure oxygen
83						.070	.061
75						.058	.053
70	1.850				.134	.050	.049
65	.750			.240	.110	.048	.045
60	.600		.436	.220	.096	.047	.040
55	.360	.333	.250	.190	.090	.042	.037
50	.275	.220	.200	.180	.084	.038	.035
45	.224	.182	.160	.147	.070	.033	.031
40	.200	.147	.120	.110	.063	.030	.027
30	.090	.084	.070	.063	.043	.028	.020
20	.060	.050	.040	.038	.027	.019	.015

The values in Table I are plotted in Fig. 2 as intensity-pressure curves. An examination of the curves shows that the intensity for pure oxygen increases proportionately to the pressure as the gas obeys Boyle's law approximately over a large range of pressure. The graph for 33.3 percent CO_2 deviates only slightly from a straight line. For larger percentages, however, the graphs show a large curvature, the intensity increasing far more rapidly than in proportion to the pressure. It can also be seen from the graphs that at any given pressure the intensity increases very rapidly with increasing percentage of CO_2. The linear relationship found by Banerji is in fact valid only at pressures not exceeding a few atmospheres.

On viewing the blue track through a double-image prism so as to have the two images side by side, the weaker image was crossed by an oblique narrow black band. A narrow slit was adjusted in front of the observation window so as to have only a part of the black band in the weaker image. The polarization measurements were then made by Cornu's method. Table II presents the results obtained for oxygen and CO_2 at 32°C.

The results are not very precise because of the depolarizing effect of the strain in the glass windows of the observation tube.

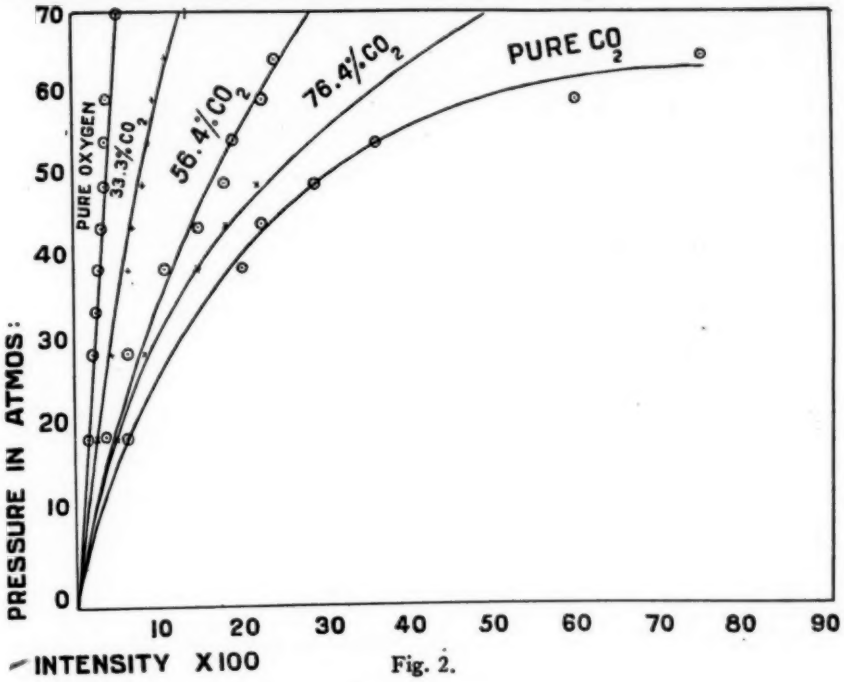

Fig. 2.

TABLE II

Polarization measurements on light scattered from oxygen and CO_2

Pressure in atmospheres	$\frac{\text{Weak component}}{\text{Strong component}} \times 100$ oxygen	$\frac{\text{Weak component}}{\text{Strong component}} \times 100$ CO_2
30	8.5	10.0
45	—	8.0
50	7.1	6.0 (R.R.*)
55	—	5.8
65	6.2	3.4
120	6.6	—

* R.R. refers to Raman and Ramanathan's value.

For pure oxygen no decided changes in the imperfection of polarization of the scattered light are observed, while in the case of CO_2 the imperfection rapidly diminishes as the pressure is increased.

In conclusion, the author's best thanks are due to Professor C. V. Raman, F.R.S., who suggested the problem and took much interest in the work.

210 BOWBAZAR STREET,
CALCUTTA.
June 15, 1926.

THE HALL EFFECT IN BISMUTH SPUTTERED FILMS

By T. F. Hargitt

Abstract

The Hall e.m.f. in sputtered bismuth films ranging in thickness from 10^{-5} to 10^{-4} cm was measured. The Hall coefficient was calculated from the usual formula, $R=Et/Hi$, and the values of R plotted against the thickness of the film. The curve shows a general increase in the value of R from 2×10^{-5} e.m.u. for a thickness of 10^{-5} cm to about 16×10^{-5} for a thickness of 10^{-4} cm.

Effect of sputtering films in a magnetic field—Three films were sputtered in a magnetic field. Two of these give values of R about 75 percent higher than for the other films of the same thickness while the third gave a value nearer that for films sputtered in the absence of magnetic field. This latter result is less determinate, however, because of the thinness of the film and the consequent smallness of R.

IN THE law involving the Hall effect it is assumed that the Hall e.m.f. is inversely proportional to the thickness of the film. The results of the experiments here described seem to indicate that for bismuth sputtered films, the law in its general form does not hold for all variations in thickness.

Preparation of the Films

The bismuth films used in these measurements were deposited by cathode sputtering on glass in a vacuum by the usual method. The cathode was formed by melting pure bismuth and casting in a graphite mold. Several forms were tried but the usual flat rectangular type was found best for the production of uniform rectangular films. The glass plate on which the films were deposited was in most cases 3.5 by 5 cm and less than a millimeter thick. The plates were chemically cleaned before the deposit was made, thus aiding in the production of films of uniform thickness. The thickness was determined by weighing.

Several methods of making contact with the film were tried but the form used in the measurements here given was the clamp contact. Brass clamps, notched for the plate were bolted to a hard rubber base plate. The ends of the clamps were wrapped with tin foil and a strip of foil was pasted to the film, under the clamps, by means of carbon paste. Cuts were made in the film parallel to the sides and running to the Hall electrodes so as to leave only a narrow strip of metal leading to the clamps.

Measurements

The usual potentiometer method of measuring the Hall e.m.f. was used. The main current of the potentiometer was furnished by a storage battery

which was checked against a standard cell at frequent intervals. The slide wire, 575 cm long, could easily be adjusted for a voltage drop per centimeter that was low compared with the e.m.f. to be measured.

The primary current in the film was furnished by storage batteries. The "cuts" mentioned above were adjusted to give an approximate balance when this current was flowing. An exact balance was secured by the adjustment of an auxiliary potentiometer. The field was then turned on and the main potentiometer adjusted for a null reading. The four possible combinations of direction of primary current and field were used and the results averaged. The total primary current varied from 6 to 50 milliamperes.

The magnet used was of the Du Bois type. The field strength, which varied from low values to 20,000 gauss, was measured by a search coil and a ballistic galvanometer. A check was made on the values so obtained by comparing them with those calculated from the change in resistance of a calibrated bismuth spiral. It was found that by placing the search coil against the pole of the magnet, slightly closer than the film, the same deflection could be secured by throwing the switch as was obtained by jerking the coil from the position ordinarily occupied by the film. This greatly facilitated the observations.

Results and Discussion

The Hall e.m.f. was measured for a number of films with variations of the primary current and constant magnetic field. The results check very well with the accepted law. Readings were also taken for a constant primary current and changing magnetic field, the values of the Hall e.m.f. being closely proportional to the strength of the field. Fig. 1 shows the Hall e.m.f. for one film plotted against the field strength.

The Hall coefficient was calculated for films ranging in thickness from 10^{-5} to 10^{-4} cm. The usual equation $R = Et/Hi$ was used where E is the Hall e.m.f. (e.m. units); i, the current per cm^2 cross section (e.m. units); H, the field strength (gauss); t, the thickness of the film (cm); R, the Hall coefficient.

Fig. 2 shows the Hall coefficient, calculated from the above formula, plotted against the thickness of the film.

It will be seen that the Hall "constant" shows a fairly regular increase with increasing thickness of the film. The points marked by divided circles represent values for films deposited in a magnetic field. The marked variation shown by two of these may have been caused by lack of uniformity in thickness.

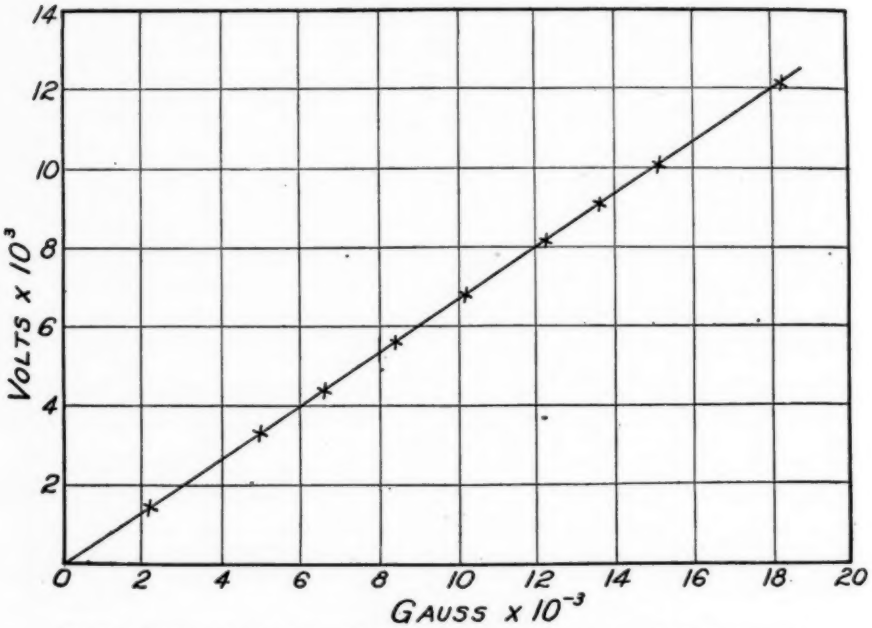

Fig. 1. Hall e.m.f. of a bismuth film as a function of magnetic field strength.

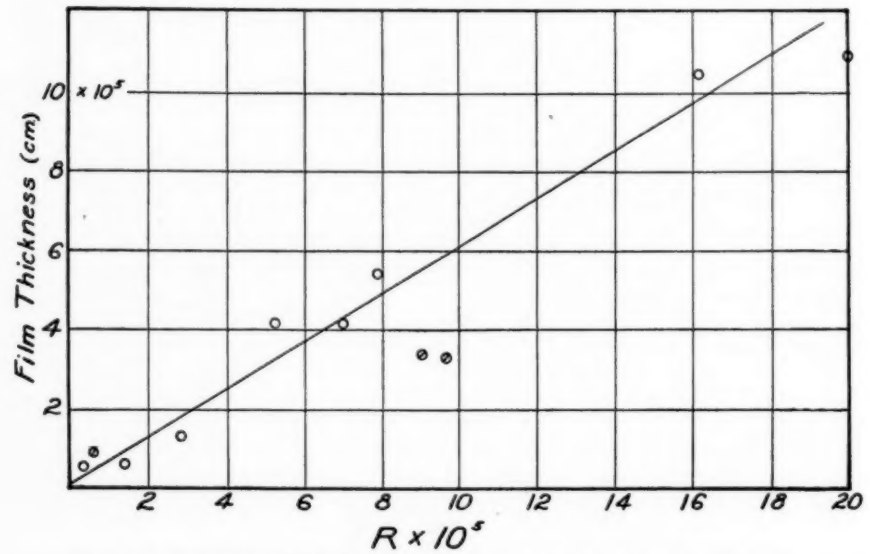

Fig. 2. The Hall coefficient of bismuth film as a function of thickness.

The fact that the Hall coefficient as calculated shows ageneral increase with an increase in the thickness of the film leads one to question whether the Hall e.m.f. is not directly proportional to the field strength and

current *density* alone ($E=KHi$) but the present data fail to establish this point. Assuming the proportionality of the Hall e.m.f. to the field strength and current density, the equivalent e.m.f. for a current density of 100 and a field strength of 10,000 was calculated. The results show a general but irregular increase of E with an increase of thickness of the films.

Table I shows the values of R calculated from the same formula as for Fig. 2 except that total current strength was substituted instead of current densities. Part of the irregularity is no doubt due to errors in determining the thickness of the plates. Perhaps the greatest source of error here is the variations in the amount of moisture on the plate. An attempt was made to eliminate this by using a dryer but great care is necessary if one does not actually increase the error in this way.

TABLE I

Values of the Hall coefficient, R, for bismuth sputtered films calculated from the formula $R=Et/HI$ where I is total current instead of current density.

Film	Thickness cm$\times 10^5$	R	Film	Thickness cm$\times 10^5$	R
1	.57	.21	7	4.0	.71
2	.8	.57	8	4.1	.53
3	.9	.30	9	5.5	.6
4*	.9	.24	10	10.6	.95
5*	3.1	1.37	11	10.8	.7
6*	3.2	1.5			

It is planned to make a more complete series of films including deposits in a magnetic field for a further study of the law involved. The writer wishes to thank Dr. A. L. Foley, who suggested this problem, and other members of the faculty of the department of Physics of Indiana University for valuable suggestions and encouraging attitude during the progress of the work.

PHYSICS LABORATORIES,
ILLINOIS WESLEYAN UNIVERSITY.

* Deposited in magnetic field. All these values of R are smaller than those given in a recent paper by P. H. Craig, Phys. Rev. 27, 772 (1926).

DIRECT ABSOLUTE MEASUREMENT OF ACOUSTIC IMPEDANCE

By G. W. Stewart

Abstract

The uniqueness of this method of measuring acoustic impedance (ratio of pressure to volume-current, lies in the fact that it involves the measurement of no other mechanical impedance, such as that of a telephone diaphragm. The computations involve values of the acoustic frequency and of the density of and sound velocity in the medium (air in this instance), and these are assumed to be known with sufficient accuracy. The only observations actually made are the readings of a centimeter scale and of relative resistances, and the disappearance of audible intensity. All measurements can thus be referred to units of mass, length and time. The method is based upon the knowledge of the effect of acoustic impedance upon the incident wave when inserted as a branch of an acoustic conduit.

Theory.—With the impedance as a branch the values of its two components can be ascertained by $Z_1=(\rho a/2S)\cdot A/(A^2+B^2)$ and $Z_2=(\rho a/2S)\cdot B/(A^2+B^2)$ wherein ρ and a are the density of and velocity of sound in the medium, S, is the area of the conduit and A and B are known functions of the incident and transmitted pressure amplitudes and of the difference of phase between them.

Method.—A common source actuated two telephone receivers, one serving as a source of sound and the other as a comparison instrument. The apparatus was so constructed that the transmitted wave was matched in intensity by one from the comparison receiver. This was done by reducing the effect of the addition of the two waves at the ears to zero. The adjustment enabled the phase relation to be measured at the same time.

Application.—Illustrations are given of the accuracy obtainable by measuring Z_1 and Z_2 for an orifice, a Helmholtz resonator and an infinite tube. Satisfactory comparisons are made with the theoretical values. The components of a conical horn are also given. The method can be used for any sort of acoustical impedance in a fluid medium and is simple, direct and accurate.

MODERN developments emphasize the importance of acoustic measurements. That of acoustic impedance is fundamental. It is herein defined as the ratio of pressure to volume-current both expressed as complex quantities, and is in fact a "point" impedance.[1] The published work on the measurement of acoustic impedance is not extensive. Kennelly and Kurokawa[2] have employed a method wherein determinations of the mechanical impedance of a telephone receiver are necessary.

[1] The definition of acoustic impedance herein adopted is to be preferred for it is convenient in acoustic theory and it is closely analogous to the accepted electrical treatment.

[2] Kennelly, J. of Franklin Inst. **200**, 467 (1925); Kennelly and Kurokawa, Proc. Am. Acad. **56**, 1 (1901); Kurokawa, Denkigakukai, 427, 1 (1924), (Translated in June 1925 issue of Q.S.T.).

The word "direct" in the title signifies that the method herein described is strictly acoustic and does not require the measurement of any other mechanical impedance. The word "absolute" indicates that all measurements can be referred to units of mass, length and time, for only the values of density of the medium, velocity of sound and of certain lengths are involved.

THEORY

A previous article[3] gives the theory of the transmission in an acoustic conduit with a branch line. The ratio of the transmitted to incident flow of energy in the conduit is independent of the nature of the branch and is given by:

$$|P'/P|^2=[(Z_1^2+Z_1\rho a/2S+Z_2^2)+(\rho aZ_2/2S)^2][(Z_1+\rho a/2S)^2+Z_2^2]^{-2} \quad (1)$$

wherein P' and P are complex pressures at the junction of the branch, the former with the branch present and the latter with it absent, Z, the impedance of the branch line, is Z_1+iZ_2, ρ and a are respectively the density and velocity in the medium and S is the area of the conduit. If measurement of the transmission, that is, of the value of (1), be made with more than one value of S, since Z_1, Z_2, and the other quantities remain constant, then it is possible to obtain values of Z_1 and Z_2.

On the other hand the following leads to a more promising method. In the theory just cited[3] we have

$$P'=P-\rho a\dot{X}/2S \quad (2)$$

wherein $\dot{X}=P'/Z$, or $\dot{X}$ is the volume-current[4] in the branch at the junction. If P and P' are respectively $P_0e^{i\omega t}$ and $P'_0e^{i(\omega t-\epsilon)}$, then from (2)

$$\begin{gathered} e^{i\epsilon}P_0/P_0'-\rho a/2SZ=1 \\ (P_0/P_0')(\cos\epsilon-i\sin\epsilon)-\rho a/2S\cdot(Z_1-iZ_2)(Z_1^2+Z_2^2)^{-1}=1. \end{gathered} \quad (3)$$

From this, if $A=(P_0/P_0')\cos\epsilon-1$, and $B=-(P_0/P_0')\sin\epsilon$ readily follows that,

$$\begin{aligned} Z_1&=(\rho a/2S)[A/(A^2+B^2)] \\ Z_2&=(\rho a/2S)[B/(A^2+B^2)] \end{aligned} \quad (4)$$

If it is possible to ascertain the ratio of amplitudes P_0 and P_0' and the difference of phase, ϵ, the values of Z_1 and Z_2 readily follow from Eq. (4).

[3] Stewart, Phys. Rev. **26**, 688 (1925).

[4] Volume-current is the time rate of volume displacement.

[5] The ratio of the pressure to volume-current per unit area, sometimes called "acoustic resistance" (see Brillié, Journal Le Génie Civil, Aug. 23 and 30, and Sept. 6 (1919)) would more appropriately be called the "specific acoustic resistance."

[6] Stewart, Phys. Rev. **20**, 528 (1922).

These formulas evidently cannot produce accurate results if ϵ is small, for when it is small, usually P_0 and P_0' are nearly equal and A, being a difference of two values closely equal, will have a relatively large error. Assuming all values in c.g.s. units, the unit of Z_1 and Z_2 might well be called the "*acoustic ohm*" until a more appropriate name can be found. Z_1 is the value of the *acoustic resistance*[5] and Z_2 the value of the *acoustic reactance*. The absolute values of Z_1 and Z_2 depend upon the measurable values of ρ, a and S.

Experimental Method

The apparatus devised to obtain the experimental values of P_0/P_0' which are required for the application of Eq. (4), is a modification of the apparatus for transmission measurements previously described.[6]

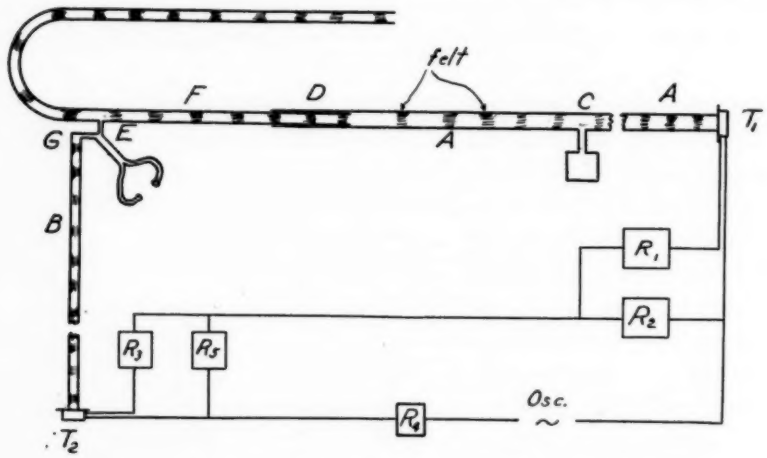

Fig. 1. The apparatus for the measurement of acoustic impedance.

The main conduit is the tube AD in Fig. 1, the source of sound a telephone receiver T_1 and the branch whose impedance is to be measured is attached at C. The tube F slides within AD. From the points E and G small branches are led to a pair of stethoscope binaurals. The tube B leads to a second telephone receiver T_2 similar to T_1. The tube B moves with the tube F as the latter telescopes into AD. The telephone receivers are connected as shown, with the filtered output of a vacuum tube oscillator used as the source of sound. The non-inductive resistances R_1 and R_3 are kept high in comparison with the impedance of the telephones. R_2 is fixed at a convenient value. The selection of dimensions of the apparatus is not important. The following measurements of length will give a sufficient description: CT_1, 274 to 84 cm; DC, 180 cm;

ED, 20 to 100 cm; GT_2, 300 cm; inside diameter of tubing, DT_1, 1.42 cm, GT_2, 1.27 cm.

Observations are taken as follows: with the branch at C removed and the hole closed, the position of the tube F and the value of R_s are adjusted until no sound is heard in the stethoscope, this condition indicating that the amplitudes from E and G are equal and opposite in phase. Then the branch is attached at C and the process repeated. The ratio of the pressure amplitudes in F in the two conditions is given by the ratio of the currents in T_2 and hence by the ratio of the two values of the non-inductive shunt, R_s. This will also be the ratio of the two pressure amplitudes at C or P_0/P_0'. From the distance between the two settings of F and the wave-length, there can be computed the difference in phase of the two waves, or the phase difference of the incident and transmitted waves at C. If d is the distance between the first position and the second, measured positively toward T_1, ϵ will be given by $2\pi d/\lambda$, wherein λ is the wave-length.

With this apparatus it is possible to make very exact settings of F and R_s over the middle range of frequencies, since, if the sound is not too greatly attenuated by the branch, one can set R_s to 0.1 of 1 percent, and obtain ϵ to a fraction of a degree. More difficulty is experienced with the very high and low frequencies, since the sound becomes inaudible over a small range. This can be remedied by using a more powerful source of sound.

The accuracy of the results obtained was highly satisfactory, but success of the method is dependent upon the precautions observed. The theory assumes that there is only one wave in the main conduit, traveling toward the left. This is a condition which was approximated in practice by using a liberal amount of damping, in the form of tufts of hair felt, in the tubes. This damping should be sufficient to absorb all but a negligible portion of the wave reflected toward T_1 by the branch at C, so that neither the vibration of the source nor the wave from it will be affected. Also there must be sufficient damping in the tube F to the left of E to prevent the wave reflected from the distant end of the tube reaching the point E again in any appreciable intensity. The first of these conditions was not approached as closely as possible since the introduction of a large amount of damping reduced the intensity of the main wave to an undesirable extent. However, measurements were taken a number of times using different lengths of tubing between C and T_1. The wave reflected from the branch and again from T_1 combined in different phases with the main wave and thus a smooth curve drawn

among the plotted values of S and transmission are probably fairly accurate. A more powerful source of sound would reduce this precaution, since it would allow the use of more damping.

A source of difficulty encountered in the measurement of values of ϵ of the order of 1°, was in the changes of wave-length in the damped tubes by small fluctuations in temperature. This was overcome by the use of asbestos steampipe covering for the tubes, and by allowing as little time as possible to elapse between the two comparison readings.

Another source of difficulty was found in the small variations of the frequency of the oscillator, which was largely eliminated by making the length of the tube B approximately equal to the distance from E to T_1, and by allowing but a short time to elapse between the two readings.

An anticipated error which did not, however, appear appreciable, was the change of the phase relation of the sound emitted by the two telephones, as the resistance R_s was altered. The two receivers were matched and kindly lent by the Bell Telephone Laboratories, Inc.

From the foregoing it is to be noticed that the electrical comparison involves merely relative values of resistances. The actual measurements are of a length, an area and the density of and velocity of sound in the medium. For all practical purposes the last two values may be regarded as known. The frequency is assumed to be given by the calibration of the oscillator.

Illustrations of Measurement

The method is applicable to any kind of branch whatsoever but in order that its use may be clearly understood, several illustrations will be cited where theoretical computations are possible. These cases may be otherwise instructive.

The orifice. In the case of the orifice, the theoretical values of Z_1 and Z_2 are[7]

$$\begin{aligned} Z_1 &= \rho\omega^2/2\pi a + (2\omega\rho\mu)^{1/2}(\pi R^3)^{-1} \cdot L. \\ Z_2 &= \rho\omega/c + (2\omega\rho\mu)^{1/2}(\pi R^3)^{-1} \cdot L. \end{aligned} \tag{5}$$

Herein, the new symbols c, L and R are, respectively, the conductivity, the thickness and the radius of the orifice. μ is the coefficient of viscosity and ω is 2π times the frequency. The results of experimentation and computation with an orifice 0.2 cm in diameter and .015 cm in length are shown in Fig. 2. The experimental curves are those of the square root of transmission, $\sqrt{T}$, or P_0'/P_0, and of ϵ. The indicated points on these two curves represent actual observations. With Z_1 and Z_2 the

[7] Stewart, Phys. Rev. 27, 487 (1926).

indicated points represent the computations by Eqs. (4) using the experimental curves of transmission and phase. The curves actually represent

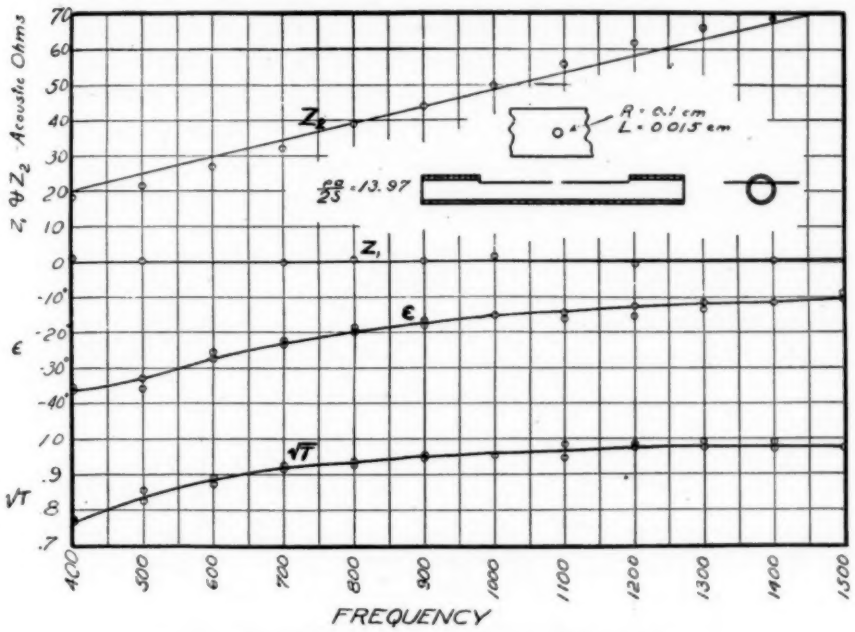

Fig. 2. Acoustic resistance and reactance of an orifice.

the values computed by the theory in Eq. (5) and are observed to be very nearly the mean of the experimental values.

The conductivity of the orifice, 0.182, is computed from the well-known expression

$$c=\pi R^2(L+\pi R/2)^{-1}$$

The accuracy of the measurements of Z_1 and Z_2 are self-explanatory, the relative error in the former being large.

In the theoretical value of Z_1, μ is neglected because of the smallness of the term involved. The radiation, which must depend upon Z_1, is shown to be exceedingly small, in fact, clearly in evidence only at the highest frequencies. In the theoretical value of Z_2 the μ term is the cause of the variation from a strictly linear function of ω. This variation is not visible in the figure.

The Helmholtz resonator. In Fig. 3 the marked points and the full line curves have the same significance as in Fig. 2. There is close agreement between the theoretical values of Z_1 and Z_2 obtained from Eq. (6) and shown on the curves and the measured values shown by the indicated

points. For $\sqrt{T}$ and ϵ the mean values of experimental data are indicated by circles, there being four series of observations with the following lengths of damped conduit between the source and the branch: 274, 285, 84 and 95 cm.

The value of ϵ is large enough to make accurate measurements possible. Z_1 is very small, and Z_2 and ϵ are practically zero at resonance. The reasons can be seen from the following equations[7]:

$$Z_1 = (2\omega\rho\mu)^{1/2}(\pi R^2)^{-1} \cdot L$$
$$Z = \rho\omega/c - \rho a^2/V\omega + (2\omega\rho\mu)^{1/2}(\pi R^2)^{-1} \cdot L. \tag{6}$$

If the μ term were zero, Z_1 and Z_2 and ϵ would all vanish at a frequency $f = \frac{a}{2\pi} \cdot (c/V)^{\frac{1}{2}}$. Z_1 is not a linear function of ω but approximately so over the range of frequencies shown. The value of c in this experiment is selected as the one which makes theory and experiment agree in regard

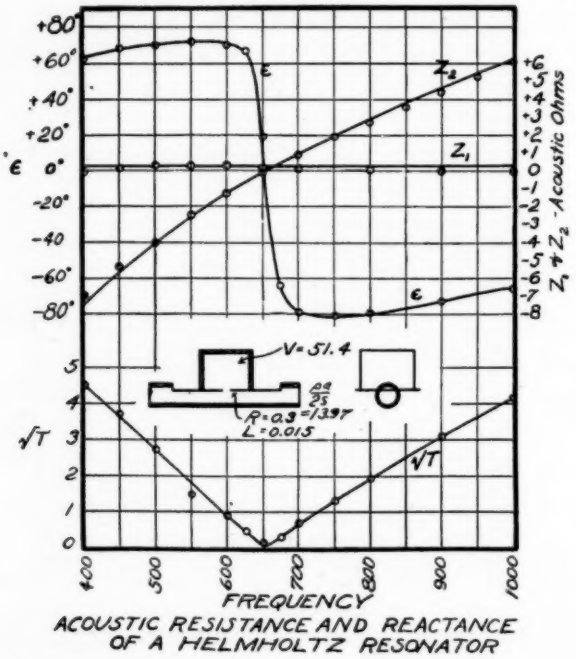

Fig. 3. Acoustic resistance and reactance of a Helmholtz resonator.

to the frequency of minimum transmission. This arbitrary selection is made necessary by the fact that, with an orifice having a diameter relatively so large in comparison with that of the conduit, the condition of location in an "infinite plane" is violated. The value computed from the usual expression for c is 0.581, whereas the selected value is 0.741.

The mean power input into the resonator at any frequency can be computed from the curves as will be shown in later illustrations. In the case of the resonator this input is very small.

The agreement between theory and experiment is remarkable. The observations of ϵ are in themselves interesting.

An infinite tube. In such a tube the ratio between the pressure and the volume current is real and is $\rho a/S$, where S is the area of the tube. If an infinite tube be attached as a branch, then there will be an inertance at the opening of $\rho\omega/c$. Therefore the values of impedances are:

$$\begin{aligned} Z_1 &= \rho a/S, \\ Z_2 &= \rho\omega/c \end{aligned} \tag{7}$$

Experimentally this case is difficult so far as accuracy is concerned, for ϵ is very small. Fig. 4 gives the results expressed as in Fig. 2. There is close agreement between the theoretical values of Z_1 and Z_2 obtained from Eq. (7) and shown in the curves and the measured values shown by

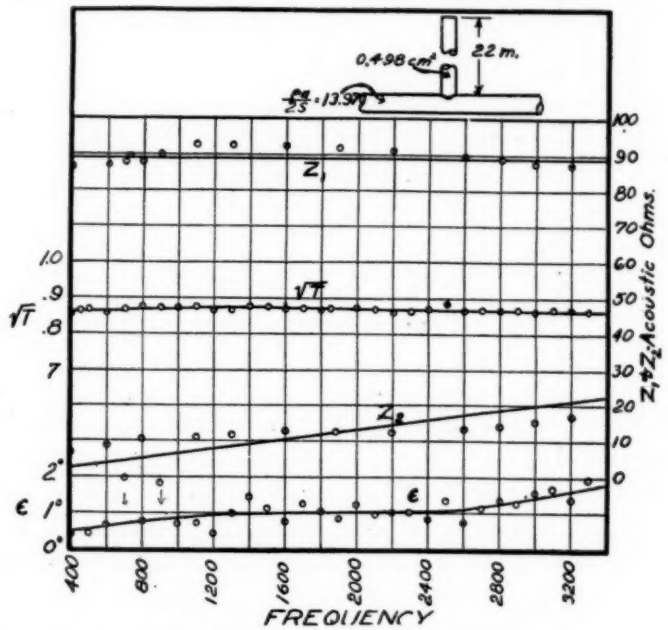

Fig. 4. Acoustic resistance and reactance of an infinite tube.

the indicated points. The "infinite tube" consisted of a tube 22 m long and 0.498 cm² in area. It seemed better experimentally to damp the vibration by the viscosity of the air, and not by the insertion of damping felt. The value of c for the opening is not the theoretical value 1.6, but

the value 1.3. This experiment illustrates the difficulty in the method when the impedance is mostly resistance. The method would be improved by the use of a known additional Z_2 in parallel with the branch. This would make the values of ϵ larger and the measurements more accurate.

The conical horn. These measurements apply to the case of any trumpet, the only condition being that its exposure is just what is expected in practice. The theoretical formulas for the values of Z_1 and Z_2 in the simplest cases are found to be complicated and exceedingly tedious in computation.

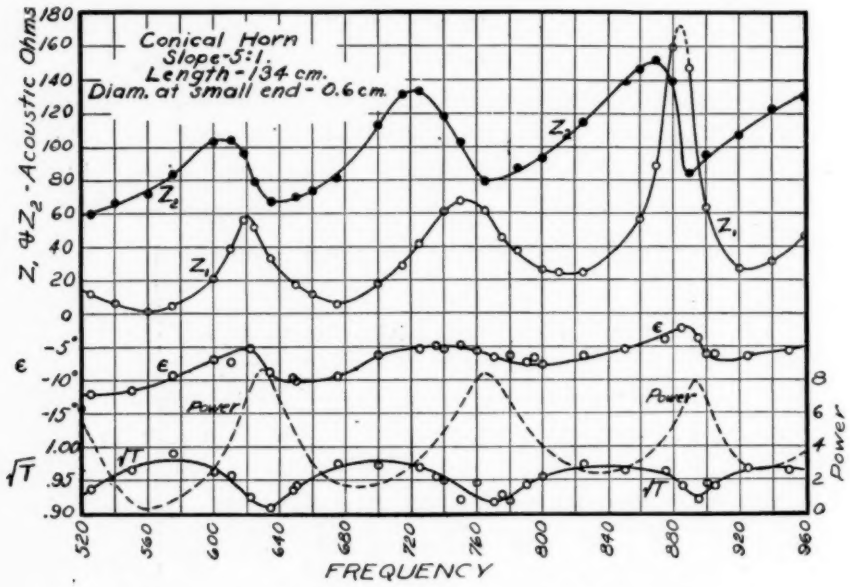

Fig. 5. Acoustic resistance and reactance of a conical horn

Fig. 5 shows the values of Z_1 and Z_2 for a conical horn as obtained from the experimental curves for ϵ and square root of transmission. The interesting technical points are: (1) Z_1 and Z_2 oscillate about ascending mean values, the former due to increased radiation and the latter due to increased inertance; (2) Z_1 has maximum and minimum values at practically those frequencies where Z_2 passes through its mean value; (3) the increase of the mean value of Z_2 may be considered as caused by the inertance at the junction end and at the exposed end, both of these increasing directly with ω but not being merely added because of the intervening complicated impedance.

It can be shown that a fair estimate of the performance of a trumpet, whether used as a receiver or as a transmitter, can be obtained from the

value of Z_1. If, for example, a fixed source, or a constant value of maximum volume current, be placed at the small end, the output is proportional to Z_1. Likewise the amplification, used as a receiver, is proportional to Z_1. In a laboratory method such as here proposed, there is a limit to the size of trumpet used, but the theory of dimensions can be invoked to enable measurements to be made upon small models. In Fig. 5 the curve indicated "power" is computed from the expression $|P'|^2 Z_1/(Z_1^2+Z_2^2)$. It is the relative power output assuming the input in the incident wave in the tube is constant.

Results of tests. The above illustrations show that the method is capable of accurate and general use where the acoustic impedance is in the medium, air. It is, however, applicable to any fluid medium.

The writer is indebted to Mr. W. D. Crozier, research assistant, for the actual tests of the method described.

HALL OF PHYSICS,
UNIVERSITY OF IOWA.
August 14, 1926.

BOOK REVIEWS

GMELINS' **Handbuch der anorganische Chemie.** Edited by R. J. Meyer.—This is the first part of an entirely rewritten eighth edition of the well known Gmelin-Kraut Handbuch. The parts are being published as separate volumes for distribution either separately or in sets. Each volume is prefaced by tables of nomenclature, abbreviations, units, constants, symbols and sources. The treatment of the subject is very comprehensive covering the occurrence, preparation, handling and all types of physical properties of He, Ne, A, Kr, Xe and Em. Not only the ordinary physical properties, but such things as optical and x-ray spectra, ionizing and radiating potentials and theories of atomic structure are included.

The work is well indexed and analytically arranged for convenient reference and cross reference. Under each topic there is given a digest, in one or two sentences of the conclusions and data of each author who has worked in the field, and generally at the end of each topic is a paragraph which summarizes the present state of knowledge in the field. The bibliography appears to be quite complete. The work should be quite useful for providing quick access to the literature and to the various constants and properties of the group of inert gases. It is, as indicated by the title, distinctly a reference work rather than a treatise. XXXII+251 pp., 6 figs., Verlag Chemie, Leipzig-Berlin, 1926.

K. T. COMPTON

La Théorie de la Relativité. M. VON LAUE. (Tome II. La Relativité Générale et la Théorie de la Gravitation D'Einstein.)—This book of 318 pages is a French translation made by Gustave Létang of the fourth German edition of Laue's treatment of the general theory of relativity. Some of the sections of the translation have been specially revised by the author. It contains a relatively complete development of the theory of general relativity, including purely mathematical chapters on tensor analysis and non-Euclidean geometry. The final chapter considers the cosmological applications of Einstein and de Sitter, and the Mie theory of matter. Pp. xvi+320, Gauthier-Villars and Cie, Paris, 1926. Price 65 fr.

RICHARD C. TOLMAN

Atomicity and Quanta. J. H. JEANS.—This little book of sixty-four pages is a reprint of the Rouse Ball lecture delivered on May 11, 1925. It contains a stimulating and attractive essay partly philosophical and partly physical. The latter part of the lecture treats the problem of the relation between wave theory and quantum theory, and will be of most interest to the physicist. The author believes that quantum rules will be found to restrict the processes of emission and absorption but not the character of radiation in free space, which will travel in accordance with the equations of the wave theory. New solutions of these equations must be found, however, which will permit the convergence of spherical waves into an absorbing atom as well as the divergence of spherical waves from an emitting atom. The treatment is full of stimulating suggestions which will be of value to any physicist who is wrestling with the baffling and fundamental problems now confronting our science.

The lecture was delivered almost simultaneously with the reports of the experimental work of Compton and Simon and Bothe and Geiger, which have greatly increased the difficulties of the wave theory, even for radiation in free space, and it will be of interest to see what modifications this will introduce in the point of view of Jeans. Pp. 64, Cambridge University Press, 1926.

RICHARD C. TOLMAN